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THE

PHYSICAL REVIEW.

THE RELATIONS OF THE PHOTO-POTENTIALS ASSUMED BY DIFFERENT METALS WHEN STIMULATED BY LIGHT OF A GIVEN FREQUENCY.

By A. E. Hennings and W. H. Kadesch.

IT is the purpose of this investigation to examine the properties of a number of metals in respect to the maximum energies of photo-electrons emitted under the influence of light of several different frequencies. Nearly all investigators who have been engaged in photo-electric studies agree that such maximum energies exist, though Ramsauer[1] has obtained results which he considers conclusive evidence to the contrary. Professor Millikan, in a recent paper,[2] has given reasons for doubting the validity of Ramsauer's conclusion. The results herewith presented, as well as those of Millikan, Richardson and Compton, Hughes, and Kadesch, all lend support to Millikan's view.

A relationship between the maximum energies of emission of electrons from different metals acted upon by light of the same frequency has been sought by several observers, but it cannot be said that one has been definitely established. Page[3] has concluded from observations on three metals, aluminum, zinc and copper, that for a given frequency the same applied potential will in the case of each of the metals examined, just prevent the escape of electrons. His conclusion, however, is not as convincing as might be desired for the reason that effects due to reflected light render uncertain the exact potential at which the electrons ceased to escape. The data in Richardson and Compton's experiments[4] indicate that for a given wave-length the value of the apparent maximum energies of emission from six of the metals examined are all approximately the same. The differences observed seem to be no larger than might be

[1] Ramsauer, Ann. der Physik, 45, p. 1121, 1914.

[2] Millikan, Phys. Rev., 7, p. 18, 1916.

[3] Page, Amer. Jour. Sci., 36, p. 501, 1913.

[4] Richardson and Compton, Phil. Mag., 24, p. 575, 1912.

accounted for by experimental uncertainties such as might be introduced, say, by variable surface conditions. Kadesch[1] using sodium and potassium and Millikan[2] using sodium and lithium, found it necessary however to apply potentials differing by as much as nearly one volt and over one half volt respectively to the illuminated plates in order to prevent the escape of electrons in the case of each of the wave-lengths used. This lack of concordance in results led Professor Millikan to suggest the present study.

APPARATUS AND EXPERIMENTAL PROCEDURE.

The photo-electric cell used in these experiments is the one designed and worked with three years ago by one of the authors in studying the relation between contact P.D.'s and photo-potentials. For a full description the reader is referred to the paper embodying the results of that investigation.[3] It will be sufficient in this place to state that the important feature of the cell is that eight metals are placed upon a wheel which, upon being rotated by means of an electromagnetic arrangement, brings the metals in succession into each of three positions. In one of

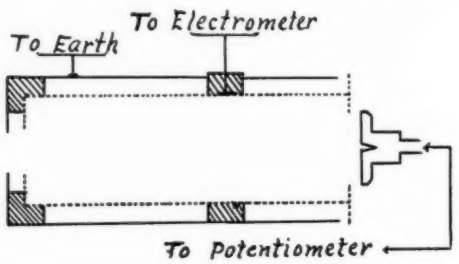

Fig. 1.

these, the photo-potentials may be measured, in another the contact potentials, and in the third the surfaces of the metals may be renewed by means of a highly tempered steel scraper operated by a second electromagnet. When in the first position the metal plate is opposite a Faraday cylinder of the form shown in Fig. 1. As is indicated, the inner gauze cylinder was connected to one pair of quadrants of an electrometer, the outer cylinder earthed, and the illuminated plate placed in communication with a potentiometer system by which the potentials applied to it were adjusted and read. The inner cylinder consisted of a double layer of fine meshed heavily oxidized copper wire netting. This blackened

[1] Kadesch, PHYS. REV., 3, p. 367, 1914.
[2] Millikan, PHYS. REV., 4, p. 73, 1914, and 6, p. 55, 1915.
[3] Hennings, PHYS. REV., 4, p. 228, 1914.

gauze was photo-electrically insensitive to wave-lengths at least as low as 2,302 Å.U. No effect due to reflected light could be detected in the case of any of the wave-lengths used.

The sensitiveness of the electrometer was about 1,400 divisions per volt. The electrostatic leak which at first was very troublesome because of the humidity during the summer months, was reduced to less than one division per minute by enclosing the photo-electric cell in a fairly tight earthed tin box, placing inside this box a tall wire-netting jar filled with calcium chloride, and forcing a stream of air already dried by passing over $CaCl_2$ into this drying jar, whence it escaped into the enclosing box.

The source of light was a mercury-in-quartz arc. A quartz lens of large aperture was used to concentrate a converging pencil of light upon the collimator slit of a quartz spectrometer. The quartz double prism was set to produce minimum deviation for wave-length 2,537 Å.U. The instrument was calibrated by means of the mercury spectrum. In adjusting the spectrometer for any desired wave-length the lines were identified by comparing the spectrum formed on a screen of uranium sulphate with a photograph of the mercury spectrum previously taken by means of the same spectrometer. Although the calibration was carefully made it was usually necessary in setting to make a slight readjustment in order to include as much as possible of the desired line in the slit of the telescope, and at the same time to make certain that wave-lengths shorter than the one desired were excluded. In making settings the collimator slit was made very narrow, but when the adjustment was completed the slit was opened to .5 mm. which was also the permanent width of the telescope slit. Since quartz lenses are not achromatic it was necessary to change the lengths of the collimator and telescope tubes for each new frequency. In order that the slit of the telescope might be at the same distance from the illuminated plate for all frequencies the spectrometer together with the mercury arc and quartz lens were so mounted that the whole system could be moved in a direction parallel to the axis of the telescope tube. The length of the collimator slit was limited by placing over it a metal screen with a horizontal opening 5 mm. wide. When adjustments were made in this way practically the whole of the surface of the metal disc was illuminated, with no light falling outside it.

The vacuum in the cell was the best obtainable. Before taking a set of observations the cocoanut charcoal bulbs attached to the system were heated to 400° C. for a couple of hours during which time a Gaede molecular pump was kept running. The bulbs were then allowed to cool, with the pump continuing to operate, and finally the system was closed

off from the pump by a stop-cock. The carbon, thus freshened, would, when surrounded by liquid air, maintain a vacuum for two days so low that no indication of pressure could be observed with a McLeod gauge sensitive to less than .000002 mm. Mercury vapor was kept from entering the photo-cell proper by gold leaf, which, loosely packed between glass wool, filled a portion of the tube leading to the cell.

New surfaces were made in vacuo by scraping the electrodes as above described. Observations on the photo-currents were taken soon after the surfaces had been prepared. Since the photo-electric properties of metallic surfaces change with time the ages of the surfaces were noted when photo-currents were being measured.

The maximum energy of electrons emitted under illumination by a given wave-length was obtained by determining the point where the "distribution of velocity" curve cuts the voltage axis. It was not necessary to plot the complete curves since it was only with the portion near the voltage axis that we were concerned. It seemed desirable to plot the points representing current in terms of the saturation current taken as unity, as well as in terms of electrometer deflections. Accordingly measurements of the saturation current were made for each metal and each wave-length.

EXPERIMENTAL RESULTS.

Six metals, magnesium, aluminum, zinc, iron, tin and copper were studied, the maximum energies of emission of electrons being determined for light of various frequencies. The spectral lines employed were 2,302, 2,399, 2,537, 2,804, 3,132, 3,342, and 3,652 Å.U. The more electronegative metals are not sensitive to the longer waves. The results are graphically represented in Figs. 2 and 3, while Table I. gives the ages in vacuo of the surfaces at the time observations were made.

TABLE I.

Age of Metals in Hours.

Wave-length.	2302	2399	2537	2804	3132	3342
Magnesium	New	½	1–½	¼	New	New
Aluminium	1	1	1	¾	¼	¼
Zinc	1–¼	½	½	¼	¼	....
Iron	1	1	½	¼	....	....
Tin	2	1–½	1	¾	....	....
Copper	1–½	1–½	1–½	1	....	....

In obtaining the data from which the curves were plotted the procedure in general was to apply to the electrode smaller and smaller accelerating potentials or larger and larger retarding ones, and to observe the

deflection of the electrometer needle, for each potential applied, due to illumination of the electrode for a chosen period of time. This was continued until the deflection had fallen to a small fraction of a

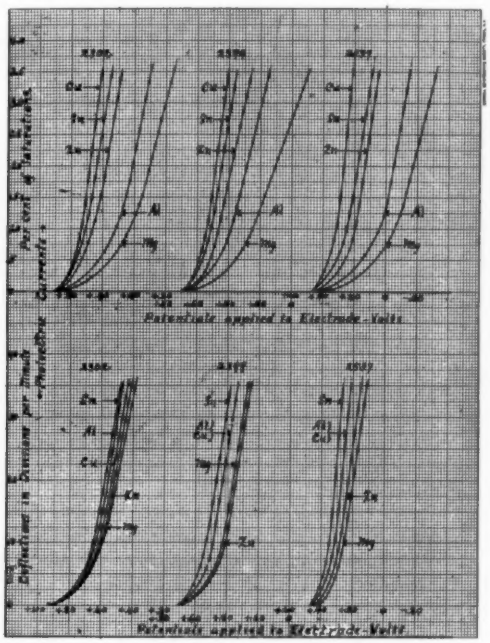

Fig. 2.

division in a minute, or had become too small to be detected. The curves are so drawn as to give all points equal weight. In fact the points fell so regularly that with the relatively heavy lines drawn they are in almost every case covered by the curves. In some cases the observations were taken in the inverse order of that given above in order to determine the lower points of the curves with surfaces as new as possible, for it became apparent when this study was under way that the observed maximum energy of emission of electrons depends on age of surface. There is a shift with time which takes place at very different rates for different metals. It would have been desirable, if possible, to determine the emission velocities corresponding to zero age. There was an objection to making observations of photo-currents immediately after scraping, however, in the fact that in general the photo-sensitiveness changed very rapidly for a time, in some cases increasing, in others falling off. Under these conditions the photo-current-potential curves would everywhere have had too great or too small a slope, and the maximum electronic

energy so determined might have been falsified accordingly. For these reasons the surfaces were not worked with until some little time after scraping. The age of each of the metals as given in Table I. is the mean age during the period of observation necessary to run the required portion of the distribution curve. That of magnesium is given as *new* in some cases. This means that the observations were begun as soon after the new surface had been formed as could be conveniently done, and moreover the lower points of the curve were located first.

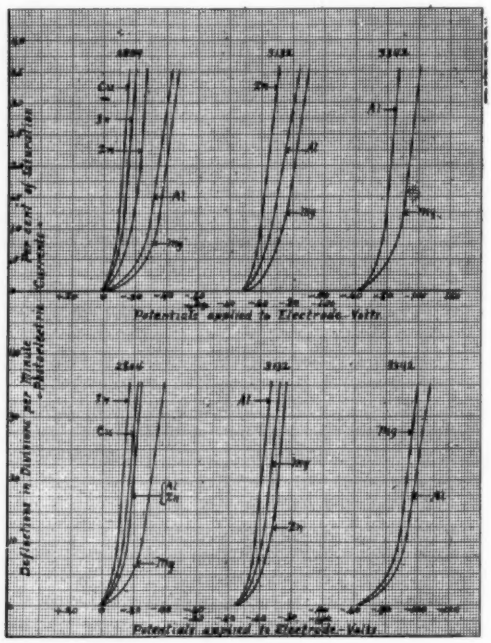

Fig. 3.

An examination of the curves in Figs. 2 and 3 shows that, when the currents are plotted as per cents. of the saturation current, they appear to emerge from a common point for each wave-length and spread out in a fan-like figure taking a definite order, viz., that of the contact potential series. In the case of the more electropositive metals the curves, on the scale here used, approach the voltage axis so gradually that it cannot be determined just where they run into it. While the curves plotted in this way show the true relation between the metals, they do not serve as well for determining the maximum retarding potentials as do those obtained by plotting the photo-currents in terms of the electrometer deflections observed in a chosen unit of time. When plotted in the latter way the

curves for the electropositive metals plunge more sharply into the axis. The order now taken by the metals is not the same as before, and is different for different wave-lengths. There is no doubt that the curves meet the axis at a finite angle, and for a given wave-length at very nearly the same point. Curves are shown for only five of the six metals examined. Those for iron were omitted for the reason that, its contact

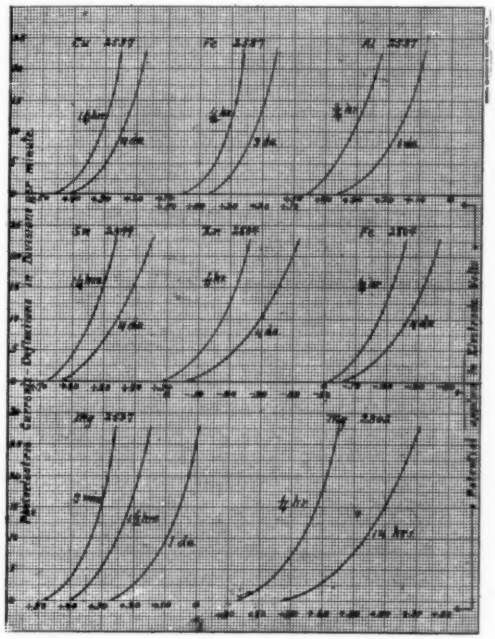

Fig. 4.

P.D. differing but little from that of tin, the two curves would very nearly coincide.

It has been noted that the age of the surface is to be taken into account. By starting observations immediately after scraping, and working very fast, a slightly greater apparent energy of emission was found for Mg and Al than for the other metals. On the other hand the curves for magnesium would have all met the axis to the right of the points for the other metals if it had been examined at an age as great as some of theirs. This is to be observed in Fig. 2 for wave-length 2,537 Å.U. in which case the magnesium surface was 1½ hours old. Fig. 4 shows how the observed maximum energies of emission of electrons shift with age of surface. Specimen curves are given for the same metal with a number of wave-lengths and also for a number of metals with the same wave-length. It is seen that

this sort of change is not peculiar to any metal or to any wave-length, but is a general phenomenon. How it may be accounted for will be considered later.

THEORETICAL CONSIDERATIONS.

The general form of Einstein's equation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - p \tag{1}$$

may be rewritten following Professor Millikan's notation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - (p_1 + p_2) \tag{2}$$

where

p_1 = work to detach electron from mother atom

p_2 = work to liberate the "free" atom from the metal surface.

The energy which just suffices to detach and set free an electron may be determined by observing the greatest wave-length to which the metallic surface is photo-sensitive. If ν_0 is this critical frequency at which electrons cease to be emitted, it follows from (2) that

$$h\nu_0 = p_1 + p_2. \tag{3}$$

The *observed* maximum energy of emission due to any given wave-length may be found by measuring either the positive potential acquired by the emittor, or the positive potential which must be applied to it, just to prevent the escape of electrons, in the presence of a Faraday cylinder the inner surface of which opposes that of the emittor. If the Faraday cylinder is electronegative with respect to the illuminated surface, the escaping electron has initially an energy greater than that corresponding to the potential observed as above. Hence, denoting by V_0, the observed maximum positive potential, and by K the contact P.D. between the opposing surfaces, we may write in view of (2) and (3)

$$(V_0 + K)e = h\nu - h\nu_0. \tag{4}$$

For another emittor excited by light of the same frequency and discharging electrons into the same Faraday cylinder

$$(V_0' + K')e = h\nu - h\nu_0'. \tag{5}$$

If the second emittor be the more electro-positive its potential is the higher by $K' - K$. Designating this as the contact P.D. between the two emittors, we find by subtracting (4) and (5) that

$$\text{Contact P.D.} = \frac{h}{e}(\nu_0 - \nu_0') + (V_0 + V_0'). \tag{6}$$

The way in which e has been introduced into the preceding equations takes care of the negative character of the electronic charge so that in this final equation h/e is to be taken as a positive ratio.

For freshly scraped surfaces, the V_0's agree so closely for all of the six metals studied that the relation

$$\text{Contact P.D.} = \frac{h}{e}(\nu_0 - \nu_0') \tag{7}$$

might well seem a general one. This is indicated also by the observations of Richardson and Compton, and those of Page. The wide differences between the apparent maximum electronic velocities observed in the experiments of Millikan and of Kadesch referred to above suggest however that this relation probably exists only for the ordinary metals.

In deducing equations (6) and (7) it was tacitly assumed that the surfaces were homogeneous, and in a steady condition; conductors, but not necessarily metallic. If films form rapidly upon surfaces thus freshly made in vacuo, and there is reason for believing that they do, then new factors are introduced which must be taken into account in interpreting the relation between the observed V_0's.

Attention has been called to the change in the apparent maximum velocity of emission of electrons with age of surface. In order to conceive a mechanism by which this change might be brought about, let us assume that a metallic surface, prepared as in these experiments in the best of vacua, does become coated with a film. Assume that this gradually increases in thickness, that it is at least partially transparent but photo-electrically insensitive to the light employed, that it does not affect the contact P.D. between electrode and Faraday cylinder, and that electrons passing through it suffer a loss in energy, which increases with increasing thickness of the film. In the presence of such a film the electron requires an additional amount of energy just to free itself. If we call this p_3, the minimum initial energy which the escaping electron must have is equal to $p_1 + p_2 + p_3$, instead of $p_1 + p_2$, and the potential necessary to prevent electrons from reaching the Faraday cylinder is equal to $V_0 - p_3/e$, instead of V_0 as in (4). Hence denoting this potential by V_0'' we have for a film coated surface

$$(V_0'' + K)e = h\nu - (p_1 + p_2 + p_3). \tag{8}$$

From this relation it is seen that as p_3 increases, V_0'' decreases. Thus a gradual shift of the photo-current-potential curves toward smaller retarding potentials may be accounted for by the formation of a film which is increasing in thickness. If the film have only the properties assumed for it above and it began forming at isolated points, spreading out from these until the entire surface were overspread, the shift would begin only when the metal became completely covered.

It is generally believed that gas films do form under the conditions

mentioned above. The properties assumed for them are just such as we should expect them to have except that perhaps they might be supposed to alter the contact P.D. between electrode and Faraday cylinder. That this would not necessarily be the case was shown by testing the effect of sheets of non-conductors on the contact P.D. when placed between an old copper surface and one of freshly polished aluminum. The contact P.D. between these surfaces in air was .87 volt. With sheets of mica and paper, and a plate of glass placed successively between, it was .91, .77 and .86 volt respectively. On repeating the observations, values slightly higher or lower than that obtained without the non-conducting sheets were found. These fluctuations were due no doubt to electrical charges on the insulators which could not be completely eliminated. We assume therefore that a gas film would probably not affect the actual contact P.D. and would not give rise to apparent fluctuation in its value, because, owing to the intimate contact between film and electrode, no residual charges would be likely to be held. It might, however, absorb energy from the electrons emitted from the underlying metal.

In addition to the inactive film assumed above it may be that others are formed which not only are photo-sensitive to light of frequencies within the range usually employed, but which also show a contact P.D. with reference to both the Faraday cylinder and the metal of which the electrode is made. If such a film exists, and is formed as we have assumed the other to be by starting at isolated points, then as long as the metal had not become completely covered there would be a non-homogeneous surface. The measured contact P.D. between this surface and any other old enough to have come to a steady condition would change progressively from that corresponding to all metal to that corresponding to all film.

How such a film would affect the potential to be supplied to the electrode in order just to prevent the escape of electrons it would be impossible, since the question as to the nature and origin of contact P.D.'s is still unanswered, to say. If these have their rise in the surfaces of the opposed conductors, depending only upon the nature of those surfaces, and being unaffected by the presence in the immediate neighborhood of other surfaces of different character then the mottling and ultimate overspreading of a metallic surface by an active film might have any one of three effects, depending upon the nature of metal and of film. If equations (4) and (5) represent the conditions for homogeneous surfaces, of film and metal respectively, and if V_0 were greater than V_0' then the potential to be applied would rise abruptly from V_0' to V_0 on the appearance of the first bit of film. If V_0 were equal to V_0' then the formation of such a film would

leave the applied potential unchanged. If V_0' were the greater, then this potential would remain unaltered until the last bit of metallic surface were covered, when an abrupt fall from V_0' to V_0 would occur.

If, on the other hand, the velocity of escape of electrons from one surface or surface element to another is affected by the presence in the near proximity of one of them, of surfaces or surface elements of a different sort, then it is possible that the potential to be applied in order just to prevent the escape of electrons from one of the component portions of a composite surface may not be at all the same as that required to prevent their escape from a surface made up entirely of this component. From the established relations of contact P.D.'s between complex surfaces it may be shown that an initially homogeneous surface upon which a film electronegative to it is forming might discharge electrons with abnormally high velocities, while the electronegative film, in the earlier stages of its formation, might discharge them with abnormally low velocities.

Although it has not been demonstrated that active films come into play in precisely the manner above postulated, there at least seems to be evidence that such exist. In the case of tin the photo-currents increased very markedly for a time after scraping, often after an hour or two reaching a maximum value as much as three times that observed immediately after the surface was made. A similar effect was noted with aluminum and zinc when the stimulating light frequency approached that of the long wave-length limit for these metals. This phenomenon has also been observed by Millikan and Souder[1] in working with the more electropositive metals. In their experiments it was even more marked than here. The falling off of the photo-currents and a subsequent change in the value of the maximum energy of emission may be due, at least in part, to the formation upon the active film of an inactive one of the sort assumed above.

SUMMARY.

The photo-current-potential curves obtained in these experiments plunge sharply into the potential axis. This indicates that photo-electrons released from a given surface under the influence of light of a given frequency have energies which do not exceed a definite finite value.

The apparent maximum positive potentials assumed by six of the common metals under the influence of light of a given frequency were the same, almost to within the limits of error of observation, so long as the surfaces had been newly scraped in vacuo. The contact P.D. between any two of these is therefore equal, to the same approximation to

[1] Millikan and Souder, PHYS. REV., 4, p. 73, 1914.

$$\frac{h}{e}(\nu_0' - \nu_0'').$$

A falling off in the maximum energy of emission of electrons was observed with increasing age of surface. This was most marked in the case of magnesium but took place to a smaller degree with all the other metals. This shift can be explained on the assumption of the gradual formation of retarding films.

In conclusion, we wish to acknowledge our indebtedness to Professor Millikan for placing at our disposal the resources of Ryerson Laboratory, and for offering valuable suggestions as the work progressed.

THE UNIVERSITY OF CHICAGO.

THE VALUE OF h DETERMINED PHOTO-ELECTRICALLY FROM THE ORDINARY METALS.

BY W. H. KADESCH AND A. E. HENNINGS.

INTRODUCTION.

AMONG the various theories of the photo-electric effect none has inspired a more active interest among physicists than that of Einstein.[1] It has been recognized that the equation

$$Ve = \frac{R}{N}\beta\nu - P \qquad (1)$$

if true, is of extreme importance. The various implications of this equation have been frequently investigated, but with no resulting unanimity of opinion as to the truth of any one of them. It is the purpose of this paper to present the results of observations made on a few of the common metals, and to draw attention to the bearing of those results on certain of the implications of the theory.

EXPERIMENTAL ARRANGEMENT, AND OBSERVATIONS.

The experimental arrangement and procedure were in the main the same as in the work reported in the preceding paper. In addition to the observations there recorded others which form the basis of the present paper were made on magnesium and aluminum. These were chosen for special study because they are sensitive to a greater range of available frequencies than are the less electropositive metals.

Owing to the presence in the beam transmitted by the spectrometer of a small amount of diffused light of all the frequencies given by the mercury-in-quartz lamp, various absorbing screens were interposed to cut out that of wave-length shorter than the spectral line desired. The effect of the more perfect monochromatism obtained in this way was to cause the potential-photo-current curves to plunge more sharply into the potential axis. The same effect was shown in a recent paper by Millikan.[2] The trailing off of the curves in the absence of absorbing screens was much less marked in these experiments, however, than in his.

In the case of magnesium five different spectral lines were used, in that of aluminum four. The latter metal, while photo-sensitive to $\lambda 3652$,

[1] Einstein, Ann. der Physik, 17, p. 145, 1905.

[2] Millikan, PHYS. REV., N.S., 7, p. 18, 1916.

gave currents so small that no accurate determinations of V for this line could be made.

A representative set of potential-photo-current curves for each of these metals is shown in Fig. 1. The points at which the curves cut the voltage

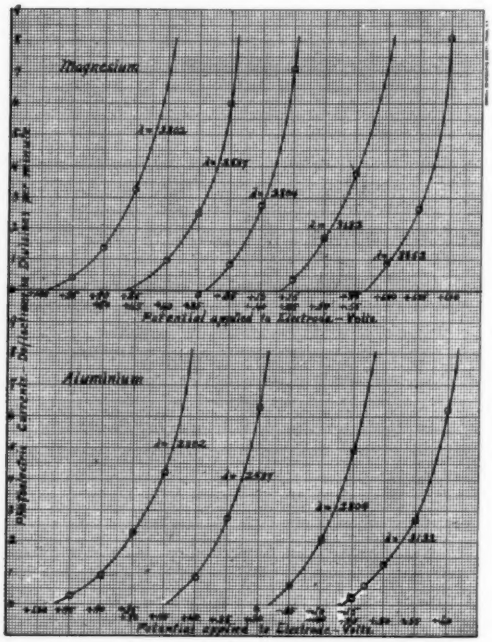

Fig. 1.

axis are taken as the apparent maximum energies of emission, measured in volts, of electrons freed by the several wave lengths. In Fig. 2, frequencies of exciting light are plotted as abscissæ; maximum emission energies in volts as ordinates. Within the errors of experiment the curve in each case is a straight line. The slopes give values for the coefficient of ν, in the above equation, of 6.45×10^{-27} and 6.41×10^{-27} for magnesium and aluminum respectively.

From the curves of Fig. 1, assuming that the points there located are correct, it would appear that there is an uncertainty of perhaps $\pm$ .02 volt in the determination of the maximum energies of emission for wavelengths, λ 2302 and λ 2537, and a somewhat smaller one for the others. The close agreement among the values of V obtained from different sets of data leads us to believe that the actual errors are in no case greater than this. Perhaps a better idea of their magnitude may be got from Table I. Under the numbers indicating the wave lengths are given the

values of V, obtained as above described, from different sets of observations.

TABLE I.

	2302	2537	2804	3132	3652
Mg.	.97 volt	.45 volt	−.035 volt	−.43 volt	−.96 volt
	.99 "	.46 "	+.02 "	−.43 "	−.97 "
			−.01 "		
Al.	.97 "	.44 "	−.02 "	−.42 "	.....
	.98 "	.45 "	−.02 "	−.44 "	.....
	.97 "	.44 "	−.01 "	−.43 "	.....
	.97 "	.445 "	+.02 "	−.45 "	.....

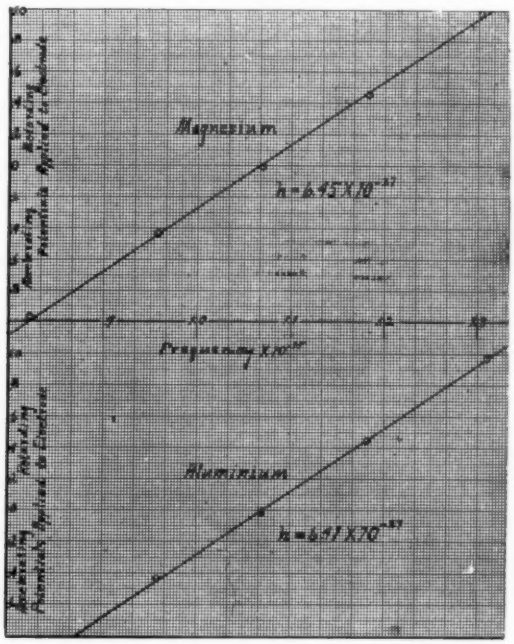

Fig. 2.

Since the experimental points do not fall accurately on a straight line, there is also a probability of error in determining the slope of the frequency-potential curve. That this need not be large is shown by the sort of agreement found among the slopes of the curves plotted for different sets of observations and by different observers. In columns 3 and 4 of Table II. are given the h's calculated from the slopes obtained by two different observers who had been asked to locate each line as accurately as possible, giving all the points equal weight, but had not been told what the V's and ν's represent. Only three sets were plotted for Al by observer A.

TABLE II.

Metal.	Set.	Observer A.	Observer B.
Mg	1	6.31×10^{-27}	6.30×10^{-27}
"	2	6.42×10^{-27}	6.38×10^{-27}
"	Average	6.37×10^{-27}	6.34×10^{-27}
Al	1	6.50×10^{-27}	6.52×10^{-27}
"	2	6.44×10^{-27}	6.52×10^{-27}
"	3	6.38×10^{-27}	6.38×10^{-27}
"	4	.....	6.38×10^{-27}
"	Average	6.44×10^{-27}	6.45×10^{-27}

DISCUSSION OF RESULTS.

The first of the assumptions of Einstein's theory is that photo-electrons emitted from a given surface under the influence of light of a given frequency have a definite maximum emission velocity. The existence of such maximum is indicated by nearly all of the photo-electric work yet done.[1] In some cases the errors due to reflected light, imperfect monochromatism, smallness of photo-currents, and perhaps other causes, such as reflected electrons and electrostatic leaks, have been very considerable. But the experiments in which these factors have been most nearly eliminated are the ones that speak most decisively for a maximum emission velocity. In contradiction with this, Ramsauer[2] concludes from his experiments that the emission velocities are grouped about a most probable value, according to some exponential law. The large and uncertain correction to be applied for the effects of "Falsches Licht," however, render the evidence on this point wholly unconvincing.

It will be seen by reference to Fig. 1 that the present experiments also indicate the existence of maximum emission velocities. All the curves approach the voltage axis quite definitely at finite angles.

It is now agreed among those who admit the existence of maximum energies of emission that these are proportional to the frequency in the exciting beam. There is no such unanimity of opinion, however, as to the way in which the slope of the energy-frequency curve varies, if at all, with the nature of the illuminated surface. According to Einstein's theory this should be the same for all.

[1] Lenard, Ann. der Physik, 8, p. 149, 1902. Millikan and Winchester, Phil. Mag., 14, p. 201, 1907. Ladenburg, Verh. d. D. Phys. Gesell., 9, p. 504, 1907. Ladenburg and Markau, Verh. d. D. Phys. Gesell., 10 p. 562, 1908. Kunz, PHYS. REV., 29, p. 212, 1909. Cornelius, PHYS. REV., N.S., 1, p. 16, 1913. Hughes, Phil. Trans. Roy. Soc., A, 212, p. 205, 1913. Richardson and Compton, Phil. Mag., 24, p. 575, 1912. Page, Amer. Jour. Sci., 36, p. 501, 1913. Kadesch, PHYS. REV., N. S., 3, p. 367, 1914. Millikan, PHYS. REV., N.S., 4, p. 73, 1914; 6, p. 55, 1915.

[2] Ramsauer, Am. der Physik, 45, p. 1121, 1914.

Hughes[1] concluded from observations on ten different elements, that among those having the same valency the slope increases regularly with diminishing atomic volume. With change of valency he found an abrupt change of slope. The values of the coefficient of ν in equation (1) calculated from his tabulated values of k, range from 5.04×10^{-27} to 6.03×10^{-27}.

Richardson and Compton[2] obtained slopes which group themselves more or less closely about two definite values. For Pt, Sn, Zn, Al, Mg and Na this was about 5.4×10^{-27}; for Cu and Bi it was about two thirds as great. One of the authors[3] obtained 6.16×10^{-27} and 6.09×10^{-27} for Na and K respectively, while Millikan,[4] for Na and Li obtained 6.561×10^{-27} and 6.585×10^{-27}. In the present experiment the values found for Mg and Al are 6.45×10^{-27} and 6.41×10^{-27} respectively. A glance at Figs. 2 and 3 of the preceding article will show that the slopes for all the other metals there studied agree within the errors of experiment with those for Mg and Al.

It is not claimed that the accuracy with which the slopes of the energy-frequency curves were determined in the present experiments is as great as in those of Millikan. The range of available frequencies was only half as great as in the case of Na. Moreover, the photo-currents were much smaller. It is thought, however, that the accuracy obtained is great enough to warrant the belief that the slopes are the same for all the metals tested. These, within the errors of experiment, are equal to Planck's h. It seems probable that other metals, whatever their nature, would yield the same result. This fact that h may be determined from the energy-frequency curve for any one of a large number of metals, of course, leaves no foundation for the conclusion reached by Sutton[5] that the product of the atomic heat of a metal by its photo-electric constant, is the same for all metals.

In comparing his values of k with h/e Hughes observes that there is no reason on the quantum theory for expecting that the slope of the frequency-potential curve should be equal to the quotient of these two universal constants. He suggests that the sharing of the energy between the electron and the parent molecule may depend on the nature of the element. It would seem, however, that the departures from this value should be accounted for in another way. It will be seen from the forms of the photo-cell employed that in his experiments the effects of reflected

[1] Hughes, *loc. cit.*
[2] *Loc. cit.*
[3] *Loc. cit.*
[4] *Loc. cit.*
[5] Sutton, Phil. Mag., 29, p. 734, 1915.

light must have been considerable. These would in every case be such as to diminish the potential to which the illuminated surface would charge up, but this effect would be greatest for the highest frequencies. The observed slope would then be smaller than it should be, by an amount which might easily be as great as the observed departure from h/e.

In the experiments of Richardson and Compton the departure of the observed slope from that predicted by Einstein's theory cannot be fully accounted for in this way. In addition to whatever errors were introduced by the back leakage due to reflected light, there would seem to have been others, due to diffused light of higher frequency than that of the spectral line desired. Both Hughes and Millikan found that the Hilger monochromators used in their experiments threw in a considerable amount of such light. Both of these observers interposed absorbing screens to cut out that of shorter wave length. No mention is made in the paper of Richardson & Compton who also used a Hilger instrument, of the use of such screens. If diffused light was present, it would have had the effect of causing the illuminated surface to charge up to a potential higher than that corresponding to the spectral line employed. This effect would have been greatest for the longest waves, so that the result in this case would also have been a diminished slope.

From the above considerations, and in view of the results of the present work and of that of Millikan, we are led to believe that when all the varied sources of error in photo-electric experiments are eliminated, or reduced to a minimum, it will be found that the slope of the frequency-potential curve is independent of the nature of the illuminated surface, and yields a value of h agreeing with that required by Einstein's equation.

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THE THEORY OF THE CATHODE FALL OF POTENTIAL.

BY H. A. WILSON.

IN the following paper the theory of the cathode fall of potential and Crooke's dark space, based on ionization by collisions of electrons and positive ions with the gas molecules and by the impact of ions on the cathode, is discussed and is shown to be capable of accounting for the main facts.

It will be convenient to begin by giving a brief statement of the experimental results of investigators on the cathode fall. F. W. Aston[1] and H. E. Watson[2] investigated the length of the Crooke's dark space and the cathode fall and found that in the commoner gases their results could be represented by the following empirical equations

$$pD = A + Bp/\sqrt{c}, \tag{1}$$

$$V = E + F\sqrt{c/p}, \tag{2}$$

where p denotes the gas pressure, D the length of the Crooke's dark space, c the current density, V the cathode fall and A, B, E and F are constants for any particular gas and cathode. The values of these constants were found for several gases and for cathodes made of different metals. The equations (1) and (2) show that the product pD and V are functions of c/p^2 only.

In Aston and Watson's experiments the current density was always larger than the value corresponding to the "normal" cathode fall which is observed when the negative glow does not completely cover the cathode.

Some important observations have recently been publisehd by C. A. Skinner[3] who has made accurate measurements of the cathode fall and length of the dark space in hydrogen. Skinner finds that the normal current density is proportional to the square of the pressure and confirms the well known fact that the normal cathode fall is independent of the pressure. He also finds that the length of the normal dark space is inversely proportional to the pressure. For current densities greater than the normal Skinner finds that pD and V are functions of c/p^2 thus confirming the results of Aston and Watson to this extent.

[1] Proc. Roy. Soc., A, 79, p. 80, 1907.
[2] Proc. Roy. Soc., A, 86, p. 168, 1912.
[3] PHYS. REV., June and August, 1915.

It appears therefore that the product pD and V are functions of c/p^2 only, in all cases including the normal values. Skinner's results for hydrogen have been shown to hold good also in oxygen and nitrogen by W. Neuswanger[1] and for cathodes of different metals by W. L. Cheney.[2]

The distribution of the electric intensity in the Crooke's dark space has been investigated by several observers. The most important results are probably those obtained by Aston[3] who measured the electric intensity by the deflection of a narrow beam of cathode rays and showed that the electric intensity was proportional to the distance from the negative glow. Thus at a point in the dark space, at a distance x from the cathode, the electric intensity is equal to $A(D - x)$ where A is a constant. This gives

$$V = \int_0^D A(D - x)dx = \frac{AD^2}{2}.$$

Aston found that the values of V directly measured agreed with $\frac{1}{2}AD^2$ and concluded that there was no sudden drop of potential close to the surface of the cathode.

Measurements of the potential in the Crooke's dark space have been made by Skinner and others by means of a fine insulated wire electrode parallel to the surface of the cathode. The results obtained in this way indicate a potential gradient increasing with the distance from the negative glow and a large drop of potential close to the cathode. Since Aston did not observe any potential drop close to the cathode it is probable, as he points out, that the exploring wire, when near the cathode, does not take up the potential of the gas. The positive ions moving towards the cathode strike the wire and give it a positive charge. In what follows I shall therefore suppose that there is no sudden drop of potential close to the cathode but that the potential gradient increases approximately uniformly from the negative glow to the cathode, as found by Aston.

Since $X = A(D - x)$ the potential V_x at a distance x from the cathode is given by

$$V_x = \int_0^x A(D - x)dx = A\left(Dx - \frac{x^2}{2}\right).$$

Let $px = y$ and put $A = 2V/D^2$ so that

$$V_x = \frac{2V}{pD}\left(\gamma - \frac{1}{2}\frac{\gamma^2}{pD}\right).$$

[1] PHYS. REV., February, 1916.

[2] PHYS. REV., February, 1916.

[3] Proc. Roy. Soc., A, 84, p. 526, 1911.

For current densities proportional to p^2, V and pD are both independent of p and therefore V_x is a function of y only. Skinner found V_x to be a function of y when c was proportional to p^2.

J. J. Thomson,[1] Townsend,[2] Skinner[3] and others have discussed the theory of the cathode fall but no complete explanation of it has been given. Townsend suggests that the gas in the Crooke's dark space is ionized by collisions with the positive and negative ions and that at low pressures electrons may be set free at the surface of the cathode by the impacts of the positive ions. He shows that the concentration of the potential fall near the cathode, due to the high velocity of the negative ions, will reduce the potential required to maintain a current to a minimum value.

Skinner supposes that the ionization in the dark space is all due to collisions of electrons with gas molecules and does not take into account ionization by collisions of positive ions. He considers that there is a fall of potential close to the cathode due to the positive ions bouncing from it. Skinner deduces from his theory that pD and V are functions of c/p^2 which agrees with the experimental results.

The existence of a smallest possible current density (the 'normal' current density) at any pressure has been explained by supposing that V has a minimum value at this current density. This explanation has been pointed out by several writers on the subject in recent years.[4]

The condition which must be satisfied, in order that a steady current may be maintained through a gas, between parallel electrodes, when the ionization is due to collisions of ions and electrons with gas molecules and when recombination and diffusion can be neglected, has been given by Townsend. If, in addition to ionization by collisions, we suppose that the positive ions striking the cathode set free some negative electrons then Townsend's condition requires modification.

Let n_1 be the number of positive ions per c.c. at a point and v_1 their velocity and let n_2 and v_2 be the corresponding quantities for the negative electrons. Let α denote the number of molecules ionized by a negative electron in moving one centimeter and let β be the same thing for a positive ion. The electric intensity X varies with the distance x from the cathode so that α, β, v_1 and v_2 are not constant. In the steady state we have, following Townsend,[5]

[1] Conduction of Electricity through Gases, 1906.

[2] Electricity in Gases, 1915.

[3] *Loc. cit.*

[4] H. A. Wilson, Phil. Mag., November, 1902, p. 614. J. S. Townsend, Electricity in Gases, p. 434, 1915. C. A. Skinner, PHYS. REV., June, 1915.

[5] Electricity in Gases, p. 429, 1915.

$$-\frac{d}{dx}(n_2v_2) + \alpha n_2v_2 + \beta n_1v_1 = 0$$

and

$$\frac{d}{dx}(n_1v_1) + \alpha n_2v_2 + \beta n_1v_1 = 0.$$

Also the current density c is equal to $e(n_1v_1 + n_2v_2)$ and is constant Substituting $c/e - n_1v_1$ for n_2v_2 we get

$$\frac{d}{dx}(n_1v_1) - (\alpha - \beta)n_1v_1 + \frac{\alpha c}{e} = 0.$$

This gives

$$\frac{d}{dx}\log_\epsilon(n_1v_1\epsilon^{\int_0^x(\beta-\alpha)dx}) = -\frac{\alpha c}{en_1v_1}.$$

Let

$$\epsilon^{\int_0^x(\alpha-\beta)dx} = Z$$

so that

$$\frac{d(n_1v_1Z^{-1})}{n_1v_1Z^{-1}} = -\frac{\alpha C dx}{en_1v_1}.$$

Hence

$$n_1v_1 = BZ - \frac{c}{e}Z\int \alpha Z^{-1}dx,$$

where B is a constant.

The number of positive ions striking the cathode per sq. cm. per sec. is equal to n_1v_1 at $x = 0$. Let γn_1v_1 be the number of electrons set free by the impacts of these positive ions on the cathode. Then at $x = 0$ we have $n_2v_2 = \gamma n_1v_1$ or

$$n_1v_1 = \frac{c}{(1+\gamma)e}.$$

This conditon gives

$$B = \frac{c}{(1+\gamma)e}.$$

Let the distance between the electrodes be S so that at $x = S$, $n_1v_1 = 0$. This gives

$$0 = \frac{c}{e(1+\gamma)}Z - \frac{c}{e}Z\int_0^S \alpha Z^{-1}dx$$

or

$$\int_0^S \alpha Z^{-1}dx = \frac{1}{1+\gamma},$$

which is the condition required. If $\gamma = 0$ this reduces to the condition given by Townsend.

In a discharge at moderately low pressures when a Crooke's dark space exists the electric intensity is very small in the negative glow so that if the positive electrode is anywhere in the negative glow then

$$\int_0^S \alpha Z^{-1} dx = \int_0^D \alpha Z^{-1} dx,$$

where D is the length of the Crooke's dark space, because α and β are both zero when X is very small. Also in the Crooke's dark space the velocity of the ions is very large so that recombination and diffusion can probably be neglected unless the current density is very large. If then we suppose that in the Crooke's dark space all the ionization is due to collisions of ions and electrons with gas molecules and collisions of positive ions with the cathode, we should expect the equation

$$\int_0^D \alpha Z^{-1} dx = \frac{1}{1+\gamma} \tag{3}$$

to hold good.

Also in the dark space

$$n_1 v_1 = \frac{c}{e} Z \left(\frac{1}{1+\gamma} - \int^x \alpha Z^{-1} dx \right), \tag{4}$$

$$n_2 v_2 = \frac{c}{e} \left(1 - Z \left(\frac{1}{1+\gamma} - \int^x \alpha Z^{-1} dx \right) \right). \tag{5}$$

We have

$$\frac{dX}{dx} = 4\pi e (n_2 - n_1),$$

which with (4) and (5) gives, putting $v_1 = k_1 X$ and $v_2 = k_2 X$

$$\frac{dX^2}{dx} = 8\pi c \left\{ \frac{1}{k_2} - \left(\frac{1}{k_1} + \frac{1}{k_2} \right) Z \left(\frac{1}{1+\gamma} - \int^x \alpha Z^{-1} dx \right) \right\}. \tag{6}$$

Let $X = pY$, $px = y$, $k_2 = K_2/p$, $k_1 = K_1/p$, $\alpha = \alpha_1 p$, $\beta = \beta_1 p$ so that (6) becomes

$$\frac{dY^2}{dy} = \frac{8\pi C}{p^2} \left\{ \frac{1}{K_2} - \left(\frac{1}{K_1} + \frac{1}{K_2} \right) Z_1 \left(\frac{1}{1+\gamma} - \int_0^y Z_1^{-1} \alpha_1 dy, \right) \right\}, \tag{7}$$

where

$$Z_1 = \epsilon^{\int_0^y (\alpha_1 - \beta_1) dy}. \tag{7}$$

In equation (7) K_2, K_1, α_1 and β_1 are all functions of Y only for Townsend has proved experimentally that α/p, β/p, v_1 and v_2 are all functions of X/p. Also y is presumably a function of X/p only, since it must depend on the velocity of the positive ions at $x = 0$.

It appears therefore that (7) is a relation between the three quantities Y, y and c/p^2. Hence we may write

$$Y = \phi \left(y, \frac{c}{p^2} \right), \tag{8}$$

where $\phi(y, c/p^2)$ denotes some function of c/p^2 and y only.

Now the cathode fall V is equal to $\int_0^D Xdx$ so that

$$V = \int_0^{pD} Ydy. \tag{9}$$

Equation (8) shows that, for a given value of c/p^2, Y is a function of y only so that pD is a function of c/p^2 only, for pD is the value of y at which Y becomes very small. Hence the equation (9) shows that V is a function of c/p^2 only. If V has a minimum value when c/p^2 is varied it follows that this minimum value will be independent of p and the corresponding values of c will be proportional to p^2 and the corresponding values of D will be inversely as p.

These results deduced from the theory are precisely those which we have seen follow from the experiments of Aston and Skinner.

If V_x denotes the potential difference between the cathode and a point at a distance x from it then

$$V_x = \int_0^{px} Ydy.$$

It follows from this and (8) and (9) that V_x is a function of y only when c/p^2 is kept constant. This also agrees with Aston and Skinner's results.

In equation (7) if we put $y = 0$ we get

$$\frac{dY^2}{dy_{(y=0)}} = -\frac{8\pi C}{p^2K_1}\left\{1 - \frac{\gamma}{1+\gamma}\frac{K_1}{K_2}\right\},$$

and if we put $y = pD$ we get

$$\frac{dY^2}{dy_{(y=pD)}} = \frac{8\pi c}{p^2K_2}.$$

Since γ is probably a small fraction and K_2 is very large compared with K_1 when Y is large, the condition at $y = 0$ is very nearly

$$\frac{dY^2}{dy_{(y=0)}} = -\frac{8\pi c}{p^2K_1}.$$

If we neglect K_2^{-1} in comparison with K_1^{-1} equation (7) reduces to

$$\frac{dY^2}{dy} = \frac{8\pi cZ_1}{p^2K_1}\left\{\int_0^y Z_1^{-1}\alpha_1 dy - \frac{1}{1+\gamma}\right\}. \tag{10}$$

The fact that V and the product pD are found to be functions of c/p^2 agrees with the theory here considered but it also agrees with Skinner's theory in which β is taken equal to zero. It appears that almost any theory making the cathode fall depend on quantities which are functions of X/p would make V and pD functions of c/p^2 only. To decide between

different possible theories it is therefore necessary to compare the observed values with values calculated theoretically.

Equations (3) and (10) represent the results of the present theory and I have therefore compared these equations with Skinner's results on V and pD, which seem to be the most reliable yet obtained.

To see if (3) and (10) agree with the experimental results the following plan was adopted. It was assumed that the electric intensity X is proportional to the distance from the end of the dark space as found by Aston. This gives

$$X = A(D - x),$$

where A is a constant and x denotes the distance from the cathode. This gives $V = AD^2/2$ so that $X = 2VD^{-2}(D - x)$. Let $X = Yp$ and $px = y$ so that

$$Y = \frac{2V}{p^2D^2}(pD - y).$$

With an aluminium cathode Skinner found the normal value of pD to be $1 \cdot 10$ and the normal value of V to be equal to 197 volts. Hence in this case

$$Y = 326(1.10 - y). \qquad (11)$$

Now Townsend[1] has determined $\alpha_1 = \alpha/p$ and $\beta_1 = \beta/p$ for a number of values of $X/p = Y$. In Townsend's experiments the electric force X was constant over the distance between the electrodes and the values of α_1 found were the values obtained when the electrons had travelled some distance in the uniform field. In the dark space the field diminishes as the distance from the cathode increases so that the average velocity of the electrons, at any point, will be greater than the velocity in a uniform field equal to the field at the point, because of the inertia of the electrons. In hydrogen at one mm. pressure Townsend found the maximum value of α to be 5 per cm. In the dark space I have therefore taken the value of α_1 at any point to be the value given by Townsend for the value of Y at a point $(10p)^{-1}$ cm. nearer to the cathode than the point in question.

Close to the cathode α must be zero because the electrons starting from the cathode cannot produce ionization until they have fallen through the minimum ionizing potential which according to Franck and Hertz is 11 volts for hydrogen. I have therefore taken α_1 to be zero from the cathode up to a point where the potential is 11 volts higher than that of the cathode. Townsend found the average ionizing potential for hydrogen to be 26 volts so I have taken α_1 to rise from zero to Townsend's value at a point having a potential 26 volts higher than the cathode.

[1] Electricity in Gases, p. 281, 320.

Fig. 1 shows graphically the values of Y, α_1, and β_1 in the dark space for the case of normal current density with an aluminium cathode in hydrogen. Y is represented by the straight line and the values of α_1

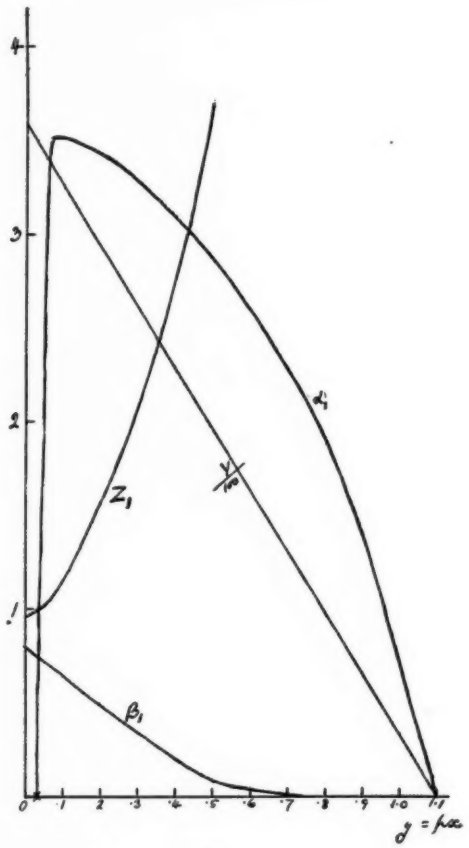

Fig. 1.

and β_1 were got from Townsend's results as just described. Townsend only found β_1 for rather small values of Y in hydrogen so that the values of β_1 for the smaller values of y had to be got by extrapolation; fortunately however a large error in β_1 makes very little difference in the results to be obtained.

The following table gives values of Z_1 and of $\alpha_1 Z_1^{-1} dy$ taking $dy = 0.1$ got from the values of α_1 and β_1 shown in Fig. 1.

The sum of the values of $\alpha_1 Z_1^{-1} dy$ is 1.009 so that

$$\int_0^{pD} \alpha_1 Z_1^{-1} dy = \frac{1}{1+\gamma} = 1.009.$$

This shows that within the limits of error γ is equal to zero in this case.

y	Z_1	$\alpha_1 Z_1^{-1} dy$
0.1	1.15	0.096
0.2	1.55	0.258
0.3	2.08	0.186
0.4	2.78	0.132
0.5	3.69	0.093
0.6	4.82	0.065
0.7	6.14	0.044
0.8	7.57	0.031
0.9	8.92	0.020
1.0	9.91	0.011
1.1	10.25	0.003

I have calculated the values of $\int_0^{pD} \alpha_1 Z_1^{-1} dy$ in the same way for the two other cases given by Skinner. In the case where the current density

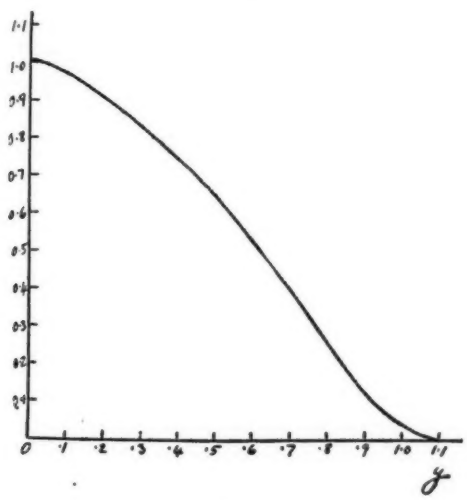

Fig. 2.

was twice normal the value of $\int_0^{pD} \alpha_1 Z_1^{-1} dy$ obtained was 1.05 and in the case of four times normal current density the value obtained was 1.10. This increase in the value of $\int_0^{pD} \alpha_1 Z_1^{-1} dy$ is, I think, probably due to the rise of temperature due to the increase in the current. The values of α_1 and β_1 used were those found by Townsend at the ordinary room temperature and α_1 and β_1 probably diminish when the temperature rises so that the values used are really somewhat too large. If the true values of α_1 and β_1 could have been employed $\int_0^{pD} \alpha_1 Z_1^{-1} dy$ would probably have

come out slightly less than unity in all three cases. As it is the fact that the calculated values of $\int_0^{pD} \alpha_1 Z_1^{-1} dy$ come out nearly equal to unity in all three cases may be regarded as confirming the theory. It appears that the assumption that the electric intensity in the dark space varies uniformly from its value at the cathode to zero at the negative glow approximately satisfies the condition

$$\int_0^{pD} \alpha_1 Z_1^{-1} dy = \frac{1}{1+\gamma},$$

if γ is supposed to be small.

To see if equation (10) is also approximately satisfied the values of $-Z_1\left(\int_0^y \alpha_1 Z_1^{-1} dy - 1.009\right)$ were calculated from the values of Z_1 and $Z_1^{-1}\alpha_1 dy$ given in the table above. The results are shown graphically in Fig. 2. It appears that this quantity varies roughly uniformly from 1.009 at $y = 0$ to 0 at $y = 1.10$. Now if $Y = A(pD - y)$ then

The values of $Z_1\left(\int_0^y \alpha_1 Z_1^{-1} dy - 1.009\right)$ for different values of y.

$$\frac{dY^2}{dy} = -2A^2(pD - y),$$

and according to equation (10) dY^2/dy is proportional to $Z_1\left(\int_0^{pD} Z_1^{-1}\alpha_1 dy - (1/1+\gamma)\right)$. It appears therefore that the assumption that $Y = A(pD - y)$ may be regarded as a first approximation to the exact solution of equation (10). The theory here proposed appears therefore to be capable of accounting for the facts in a satisfactory way.

At $y = 0$ we have approximately

$$\frac{dY^2}{dy} = -\frac{8\pi c}{K_1 p^2}.$$

Putting

$$\frac{dY^2}{dy} = -2A^2 pD$$

this gives

$$K_1 = \frac{4\pi c}{A^2 D p^3}.$$

We have also $A = 2V/p^2D^2$ so that

$$K_1 = \frac{\pi c (pD)^3}{V_s^2 p^2}.$$[1]

[1] A similar equation to this was obtained in a quite different way by Aston, Proc. Roy. Soc., A, 79, p. 80, 1907.

The following table gives the values of pD, c/p^2 and V found by Skinner and the calculated values of K_1. c is in milliamperes per sq. cm., D in cms., and p in mms. of mercury.

c/p^2	pD	V	K_1
0.0742	1.10	197	7.2×10^3
0.1484	0.844	204	6.1×10^3
0.2968	0.624	227	3.9×10^3
			Mean, 5.7×10^3

The values of K_1 are for one volt per cm. at one mm. pressure. The mean result gives 7.5 cm. per sec. for one volt per cm. at 760 mm. pressure, which is nearly equal to the velocity of positive ions in hydrogen at 760 mm. as found by Zeleny, Langevin and others. This confirms the conclusion that the velocity of the positive ions is inversely as the pressure down to pressures of the order of one mm.[1]

The above theory becomes, in principle, similar to the chief part of Skinner's theory if we take $\beta_1 = 0$. The values of α_1 assumed by Skinner are however much larger than those found experimentally by Townsend but this does not affect the form of the theory.

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[1] Aston, Proc. Roy. Soc., A, 79, p. 80, 1907. H. A. Wilson, Proc. Roy. Soc., A, 79, p. 417, 1907. Lattey and Tizard, Proc. Roy. Soc., A, 86, p. 349, 1912.

THE INFLUENCE OF OCCLUDED GASES ON THE PHOTO-ELECTRIC EFFECT.[1]

BY ROBERT JAMES PIERSOL.

THE part played by the gaseous films and occluded gases in the photo-electric effect has been studied by many investigators, who have not reached consistent conclusions.

Cantor[1] and Knoblauch[2] found that reducing agents and bodies not fully oxidized lose a negative charge rapidly when illuminated by ultra-violet light. Oxidizing agents and bodies which are oxidized do not lose a negative charge. Since a metal seems to give off more photo-electrons during oxidation, they concluded that the photo-electric effect is due to oxidation of the surface illuminated by ultra-violet light.

On the other hand, Chrisler[3] holds the view that hydrogen is essential to the photo-electric current, so that if it were possible to remove all occluded hydrogen there would be no photo-electric effect. Hydrogen has a very high coefficient of diffusion. Hence it is difficult to remove all occluded hydrogen from a metal. Palladium, in particular, has a high power of absorption for this gas.

Kustner[5] found that there seems to be no evident photo-electric effect in zinc after it had been scraped in vacuo. He took precautions to exclude all active gases from the metal.

Wiedemann and Hallwachs[6] supposedly removed the occluded gases from potassium by seven consecutive distillations, which seemed to cause the photo-electric effect to disappear entirely. Fredenhagen[7] confirmed these results in a similar series of experiments. Stumpf[8] obtained results by heating palladium electrically, from which he assumed a final zero effect. Paech[9] found that the photo-electric effect of a metal is dependent upon the gases which may be occluded such as oxygen, hydrogen, carbon dioxide, helium and argon.

[1] Accepted by the University of California in partial satisfaction of the requirements for the degree of doctor of philosophy.

[2] Wien. Sitzunger., 102, p. 1138, 1893.

[3] Zeit. f. phys. Chemie, 29, p. 527, 1899.

[4] PHYS. REV., 27, p. 267, 1908.

[5] Phys. Zeits., 2, p. 68, 1914.

[6] Verh. d. deut. phys. Ges., 2, p. 107, 1914.

[7] Verh. d. deut. phys. Ges., 5, p. 201, 1914.

[8] Verh. d. deut. phys. Ges., 22, p. 989, 1914.

[9] Ann. d. Phys., 43, p. 35, 1914.

On the contrary, Pohl and Pringsheim,[1] experimenting with potassium in vacuo, found that it behaved in practically the same way after repeated distillations. This would seem to show that there is an intrinsic photo-electric effect which is independent of occluded gases.

Hennings[2] studied the mutual relations of contact potential and the photo-electric properties of metals in vacuo, using a revolving knife edge to scrape new surfaces within the vacuum. His results show "(*a*) metals are more electro-positive when scraped in vacuo, but gradually become electro-negative with time; (*b*) photo-electric sensitiveness is increased by the removal of surface films; and (*c*) without films the photo-electric sensitiveness agrees exactly with the order of the Volta contact series."

Hughes,[3] in studying the contact difference of metals, has shown that initially there is but little contact difference of potential between distilled bismuth and zinc, as compared with platinum. A trace of admitted air greatly increased this difference. He showed that the change is located at the surface which becomes electro-positive.

Hartley[4] attempted to ascertain the electrical condition of a gold surface during the absorption of gases. The use of gold is favorable because it does not form chemical compounds easily. He showed that "(*a*) the gold surface acquires a negative charge during the catalytic combustion of gases in contact with it; (*b*) the electrical effect is antecedent to the actual combustion and primarily is due to the occlusion of gases; and (*c*) the metal becomes negatively charged during the removal of occluded hydrogen and positively charged during the removal of occluded oxygen."

Stoletow[5] found that the photo-electric effect increases in heating platinum to 200° C., but his results are complicated with secondary maxima and minima.

Zeleny[6] showed that the photo-electric effect of a heated platinum wire at first diminishes, reaching a minimum between 100° C. and 200° C., and subsequently increases to about 700° C., where its value is twice that at room temperature.

Varley and Unwin[7] confirmed these experiments, heating platinum foil.

Millikan and Winchester[8] studied the influence of temperature on photo-electric effects in high vacuum. Below 125° C., rise of tempera-

[1] Verh. d. deut. phys. Ges., 7, p. 336, 1914.
[2] PHYS. REV., 3, p. 228, 1914.
[3] Phil. Mag., 27, p. 170, 1913.
[4] Roy. Soc. Proc., 90, p. 9, 1914.
[5] Comptes Rendus, 108, p. 1241, 1889.
[6] PHYS. REV., 12, p. 321, 1901.
[7] Roy. Soc. Proc., 27, p. 117, 1907.
[8] Phil. Mag., 14, p. 188, 1907.

ture did not effect nickel, silver, gold, copper, iron, zinc, lead and aluminum.

Millikan[1] found that for sodium an equilibrium condition took place in the contact difference of potential about an hour after it had been cut in a vacuum of about 0.001 cm. of gas pressure. This constant potential was accompanied by constant and very large saturation currents. He assumed that this constant state was due to a state of equilibrium of the occluded gases.

Ladenburg[2] investigated platinum, gold and iridium in a very good vacuum at high temperatures. He found a maximum about 100° C. By heating and cooling several times in succession, this maximum effect disappears almost entirely. He attributes this to water vapor. Also he supposes that an increase near 800° C. is due to resonance.

The purpose of this investigation was to obtain definite data which will give additional light on the fundamental nature of the photo-electric effect. There was a desire to establish the relations of the saturation current with respect to occluded gases. We shall define the saturation current as the maximum value of the photo-electric current obtained by an electric field of sufficient gradient to sweep all the negative electrons to the receiving electrode. The data will increase the evidence as to whether the photo-electric effect is due to (*a*) an intrinsic property of the metal; (*b*) a surface film due to the oozing out of occluded gases; or (*c*) both an intrinsic property of the metal and a secondary effect due to gaseous films.

The apparatus, as shown in Fig. 1, consists of a heavy brass vacuum case *A*, put to earth. Coaxial with the case, a brass gauze cylinder *B* is supported by the rod *C*. The cylinder is copper-plated so that it may be blackened by oxidation. The metallic strip *D* is supported by the brass terminals *E*, which pass through a ground glass joint *F*. The terminals end in mercury cups, to which may be connected either the secondary of a transformer or any desired potential. In series with the primary of the transformer there is a choke-coil so calibrated that there is a scale which reads the amperes passing through the metallic strip. A circular quartz plate *G*, 0.1 cm. in thickness and 2 cm. in diameter, ground with its optical axis perpendicular to its surface, serves to transmit the ultra-violet light. The source of illumination is a mercury vapor lamp, focused on the metallic strip by a quartz lens. The receiving gauze cylinder is connected through a key *H* to a quadrant electrometer *I*, which has a sensibility of 50 divisions per volt on a scale at a distance of

[1] PHYS. REV., 3, p. 355, 1916.

[2] Verh. d. deut. phys. Ges., 9, p. 165, 1907.

one meter. The key is as shown, with a Victrola needle J, put to earth, which makes connection with a soft iron plate K, supported by a sulphur column, fixed to a solid iron base. The glass window L assists in focusing. The opening M leads to a Gaede rotary mercury pump, which gives a desired vacuum, less than 0.0002 cm. of mercury pressure, read by a McLeod gauge. The metallic strip is 1.5″ (3.809 cm.) in length, 0.5″ (1.270 cm.) in width, and 0.002″ (0.005 cm.) in thickness.

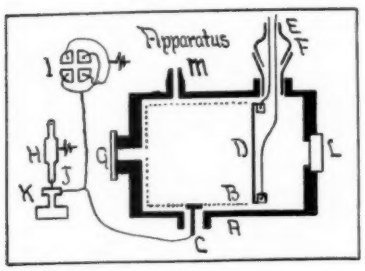

Fig. 1.

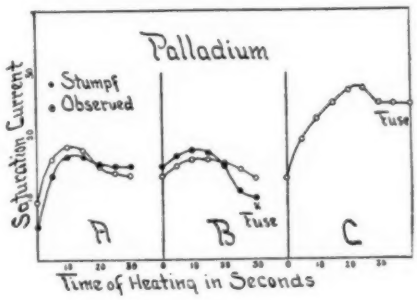

Fig. 2.

Preliminary experiments were made with palladium in order to verify Stumpf's results. He used the method of repeated heatings at increasing temperatures. By using arbitrary heating currents through the palladium, results were obtained as shown in Fig. 2. Divisions A, B and C of the figure represent successive increases of heating current. Each observation was taken after the occluded gases were pumped out for 5 minutes, the strip having been heated for 5 seconds. It may be noted that the sensibility of the final reading x, which Stumpf observed, was about twice the magnitude of the initial condition before heating. Yet he assumed that he would have reached a final zero value, due to the slope of the curve at x, with additional heatings, if the strip had not fused. It was possible to heat the strip at a higher temperature as shown in division C. Much difficulty was due to the sputtering effect, which decreased the thickness of the strip, therefore in order to heat the strip to the same temperature it was necessary to diminish slightly the heating current at each heating. The data for higher temperature would seem to indicate that the conclusions of Stumpf were not final.

There was a desire to establish the relation of the pressure of gas emitted to the photo-electric current. In Fig. 3 curve A and curve B This suggests that there may be a relation between the amount of gas driven off by heating and the saturation current. It is possible that the heavier occluded gases are driven off between 30 and 50 amperes, causing show the saturation current and pressure of emitted gas respectively as

plotted against heatings at increasing amperage. The saturation current was measured in divisions of deflection per second of the electrometer. Before each heating the pump was stopped and immediately after heating the increase of pressure was measured by a McLeod gauge. Then the gas was pumped out for 5 minutes, after which the saturation current was measured. A marked similarity exists between the two curves.

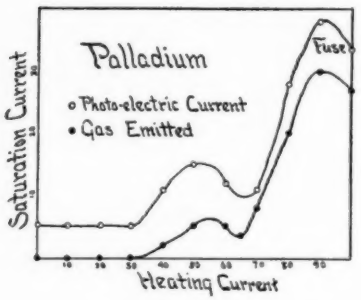

Fig. 3.

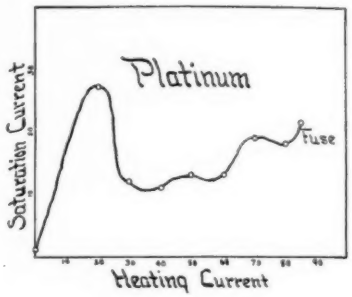

Fig. 4.

an increasing saturation current. Practically all these heavier gases escape below 65 amperes. This inactive condition of the occluded gases causes a decrease in current. Then the lighter gases begin to escape, and there are changes until all these gases are removed at about 90 amperes. Attempts were made to verify this point experimentally by spectrum analysis of the gases emitted at each temperature, but the work was brought to an end for the present, due to my departure from the university to pursue other work.

In the final results extreme care was taken to exclude from the system all stop-cock grease and water vapor. The metallic strips were handled with care so as to keep them free from any impurity. The sensibility of the electrometer remained constant (50 divisions per volt.) Between series of experiments it was necessary to re-focus the ultra-violet lamp, so that it may be necessary to multiply the magnitude of the saturation current by a constant due to a possible change in intensity of light, should it be desired to compare the values for two different metals. But the saturation currents for each series are absolutely comparable. The potential of the heating current is 10 volts, with a range from 0 to 250 amperes. All heatings were for a period of 10 seconds, the emitted gas being pumped out for 5 minutes before each observation was taken. A field of 100 volts was kept between the emitting and receiving electrodes to insure a saturation current.

The effect of heating platinum is shown in Fig. 4. The one striking characteristic is the large magnitude of the saturation current at 20

amperes. Fig. 5 shows the same series with a new piece of platinum with numerous readings near the sudden increase. This confirms the previous curve. Fig. 6 shows the effect of repeated heating of the same piece of

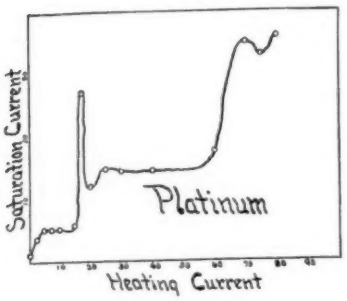

Fig. 5.

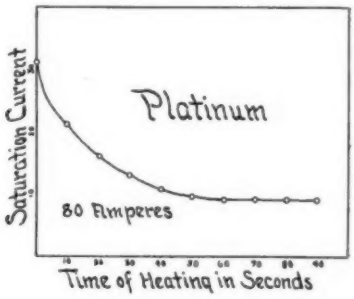

Fig. 6.

platinum immediately after the last experiment, without receiving the strip from vacuum. This gives evidence that the saturation current drops to a constant value with repeated heating to the temperature due to 80 amperes, which is very near the fusion point. In order to confirm this constant saturation current value, a new piece of platinum was heated at 80 amperes, 60 times in vacuo, to drive off all occluded gases possible. Then a series of observations were taken with increasin heatings from 0 to 80 amperes in order to ascertain if the sudden increase in the region of 20 amperes still existed. Fig. 7 shows that the condition which caused the sudden increase, together with the other irregularities, has been removed. This would seem to show that no more occluded gases were driven off at a temperature below the fusion point. The close agreement of the values for the saturation current is more apparent when tabulated as shown in the original form in the following table:

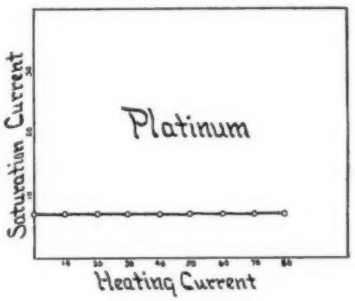

Fig. 7.

Amp.	Div.	Sec.	Div./Sec.
0	20	2.8	7.1
20	20	2.8	7.1
30	20	2.9	6.9
40	20	2.8	7.1
50	20	2.9	6.9
60	20	2.6	7.4
70	20	2.8	7.1
80	20	2.8	7.1

The effect of heating gold is shown in Fig. 8. Gold has a low point of fusion (60 amperes) which is the temperature region of initial maximum emission of gases. A new piece of gold was heated 35 times at 60 amperes, when it seemed to have come to a constant value. Fig. 9 shows that

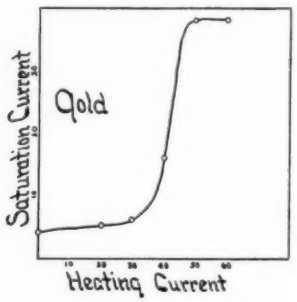

Fig. 8.

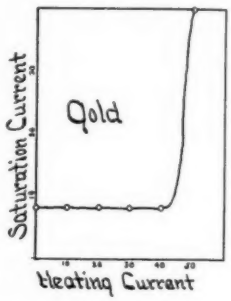

Fig. 9.

sufficient occluded gases still remain in the gold to give unstable conditions at the critical temperature of gas emission. In a continuous experiment the gold was heated 15 times at 50 amperes. The saturation current continued to increase.

The characteristic irregularities of nickel are shown in Fig. 10. Fig. 11 shows the results of a second series of readings with a new piece of nickel, observed in order to establish the maximum condition at 20

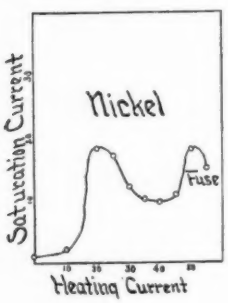

Fig. 10.

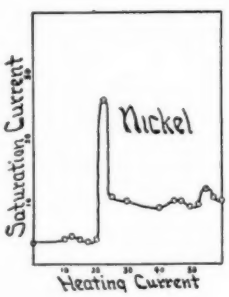

Fig. 11.

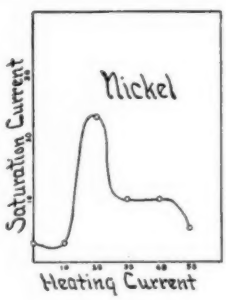

Fig. 12.

amperes. Fig. 12 shows the next series, with new nickel, which was obtained by driving off the occluded gases at each temperature until a constant value for that temperature was obtained. The heating was repeated 15 times at 20 amperes. The final constant values are shown. This seems to establish the conclusion that, below a critical temperature, repeated heating does not drive off all the gas, but some remains active at the surface of the metal. In a continuous experiment the same piece of nickel is heated 8 additional times at 50 amperes. Fig. 13 shows the results for heatings at increasing temperatures.

The effect of absorption was studied in order to determine whether the maximum saturation current is due to the emission rather than the absorption of gases. After the strip of nickel had been heated at the critical temperature due to 20 amperes, it was permitted to absorb gases under atmospheric conditions for given periods of time. Before each absorption the apparatus was evacuated in order to determine the saturation current. The following table shows the results.

	Absorption Div./Sec.
0 sec.	32.6
5 min.	29.2
10 min.	25.4
15 min.	25.0
22 hrs.	17.6
30 hrs.	12.4

After the final reading the nickel was heated at 20 amperes. The maximum effect increased to 6 times the maximum effect due to first heating. This might suggest that the nickel occluded more gases after the process of heating.

Fig. 14 shows the results of heating palladium. A new piece of palladium is heated 8 times near fusion when a constant value is reached.

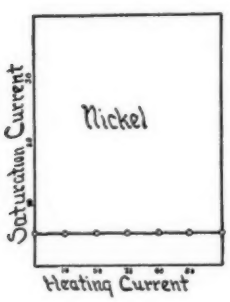

Fig. 13.

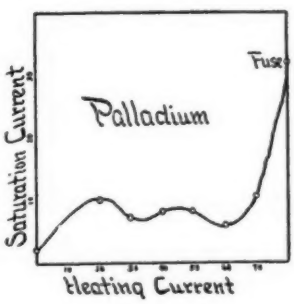

Fig. 14.

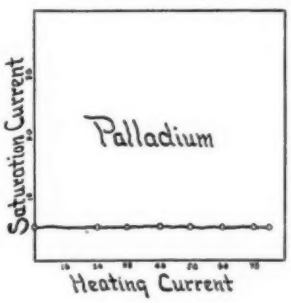

Fig. 15.

Fig. 15 shows that the saturation current is constant with respect to increasing temperature.

The influence of occluded gases on the photo-electric effect of silver is shown in Fig. 16. Although silver fuses at a lower temperature than gold, yet it was found to be possible to drive off the gases causing the maximum saturation current with 25 heatings. The results are shown in Fig. 17.

In a discussion of the results it is interesting to note that the method of heating metallic strips electrically in vacuo presents an easy and efficient method of cleaning the surface of the metal. This is true especially

in metals like palladium where the sputtering effect occurs at high temperatures. At each heating the surface is renewed. Also the high temperature tends to break down any existing gaseous surface film, the gas of which is pumped from the system.

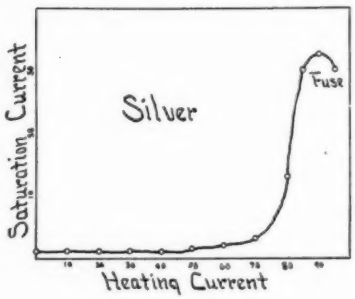

Fig. 16.

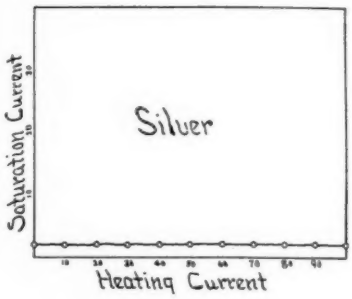

Fig. 17.

It is evident that the spurious effects are due to the gas driven to the surface rather than to the absorption of gas. At the critical temperature of maximum effect, the occluded gas is forced probably only to the surface, but is not ejected entirely. This is perhaps the reason why increased heating is necessary to remove the maximum effect.

These results give a valid proof for the assumption that the variation of the photo-electric effect with temperature is due to occluded gases. The maxima and minima of the photo-electric effect are due to occluded gases, corresponding to the maxima and minima of the photo-electric effect due to temperature as found by Ladenburg. This suggests that the effect of temperature on the saturation current is primarily an effect of the activity of the occluded gases at that temperature.

In this investigation of the influence of occluded gases the results are not confused by experimental conditions with the thermionic effects which are superposed on the photo-electric effect at high temperatures. This is because the observations were made after the metal was cooled to room temperature.

It does not seem probable that the maxima near 100° C. are due to water vapor as suggested by Ladenburg. The work was pursued at low pressures rather than under atmospheric conditions. Also there is no final increase at high temperature, necessitating explanation by a resonance theory.

The results due to the fact that gold fuses near the initial maximum, are of value in as much as they show that the occluded gases causing the abnormal increases in other metals have been removed. If the occluded gases were still present the critical effect would be permanent, as in gold.

Experimental data seem to give definite evidence in support of the following conclusions:

1. A photo-electric effect exists which is due entirely to an intrinsic property of the metal.

2. Superposed on this effect there is a maximum effect due to occluded gases.

3. The maximum effect is dependent upon the activity of the gaseous surface film (its magnitude being a function of the amount of gas driven to the surface).

4. The abnormal effects are due to the emission rather than the absorption of occluded gases.

5. In metals of high fusion point, a sufficient number of heatings drive off the occluded gases to such an extent that all abnormal effects disappear.

6. The photo-electric sensitiveness, after the emission of occluded gases, is larger than the effect noted before the expulsion of the gas.

Finally, it gives me pleasure to acknowledge the kindly suggestions of Professor E. P. Lewis, under whose direction the work has been pursued.

Department of Physics,
University of California.

NOTE ON THE PARSON ELECTROMETER.

BY G. E. M. JAUNCEY AND G. J. BUCHNER.

A. L. PARSON[1] has described a modification of the quadrant electrometer in which the quadrants are replaced by sectors, the angle of each sector being about 70 degrees, and in which the needle is suspended over the sectors which are plane and not of the box form as in the ordinary quadrant electrometer. The sectors are mounted on a pair of arms pivoted scissors-like at the center.

The needle being suspended by a nearly torsionless fiber and the two pairs of opposite sectors being at zero potential, the needle sets itself in a symmetrical position with its axis half-way between adjacent pairs of sectors as shown in Fig. 1. If the gap between the sectors is widened

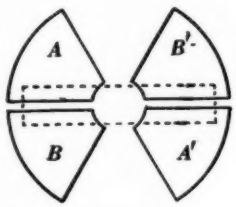

Fig. 1.

then the needle becomes unstable and it is just when instability is approached that the instrument becomes very sensitive. Besides setting itself in a symmetrical position the needle may set itself in an unsymmetrical position such that the axis of the needle nearly corresponds with the axis of one pair of opposite sectors.

The authors, using a similar instrument, have obtained the following interesting curves for the deflection of the needle when in the unsymmetrical position. In the instrument used the angle turned through by the opposite sectors AA' when A was moved from a position near B to a position near B' was 32.5 degrees. The ordinates represent the deflection of the needle for a voltage given by the number printed above each curve and the abscissæ represent the difference of the angles between the sectors when adjacent sectors are in a given position and when they are close

[1] PHYS. REV., Second Series, Vol. VI., No. 5.

together. It is notable that all the curves cross the axis of angles at the same point, namely 4.4 degrees.

The needle was charged throughout the experiment to + 150 volts.

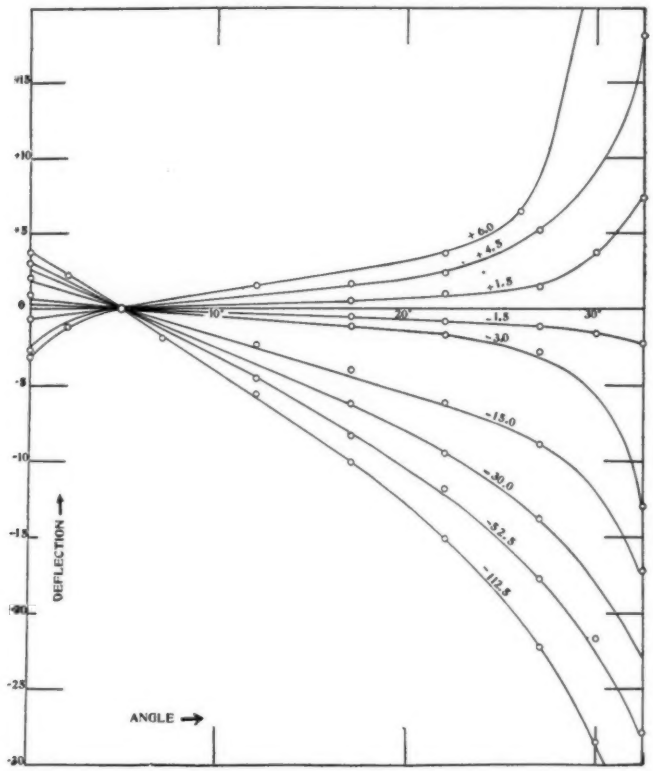

Fig. 2.

The authors desire to thank Professor MacNutt for his interest in this work.

PHYSICAL LABORATORY,
LEHIGH UNIVERSITY,
May, 1916.

THE BLACK BODY AT THE MELTING POINT OF PLATINUM AS A FIXED POINT IN PHOTOMETRY.

BY HERBERT E. IVES.

SEVERAL attempts have been made to utilize platinum in connection with the establishment of a standard of luminous intensity. Of these perhaps the best known is that of Violle,[1] who proposed that the unit of light should be the amount of light given out by unit area of platinum at its melting point. Certain objections, theoretical and practical, stand in the way of such a standard. From the theoretical side, it is undesirable that such an entirely accidental or arbitrary thing as the melting point of any substance should determine the dimensions of a scientific standard. The standard of luminous intensity should be fixed, as closely as may be, in terms of the c.g.s. system, instead of in terms of fuel composition or melting point. The *watt of luminous flux*, as defined and evaluated in recent investigations,[2] meets this theoretical requirement.

On the practical side great difficulty has been experienced in evaluating the Violle standard. The chief obstacle appears to be the condition of the surface of the molten platinum. This is highly reflecting, and at the same time subject to variations due to contamination.

Several years ago Waidner and Burgess[3] proposed a notable improvement on the Violle standard. They suggested that instead of taking the platinum surface as the light source, a black body at the temperature of melting platinum be substituted. The great advantage of the black body is of course that it has no "surface" to reflect or become contaminated. They discussed several ways in which this proposal could be carried out practically, some involving rather costly apparatus or investment in platinum. Nothing further has been done by them, however, toward working out this very vital improvement in the Violle idea.

The proposal of Waidner and Burgess in their own words is as follows:

[1] J. Violle, "Sur l'etalon absolu de lumiere," Annales de Chemie et de Physique, (6), 3, p. 373, 1884.

[2] A Review and Bibliography of this subject is to be found in the Journal of the Franklin Institute, Oct., 1915, p. 409.

[3] Waidner and Burgess, "Note on the Primary Standard of Light," Electrical World, Sept. 19, 1908, p. 625.

"The unit of light may be defined as the intensity of the light emitted (white or monochromatic) by one square centimeter of a black body at the temperature of solidification of platinum."

It will be noted that while the practical objections to the Violle standard are removed by the substitution of the black body for the platinum surface, the theoretical one raised above still remains. Such a standard is subject to the general criticism of all standards proposed until recently, that it would have no logical connection with any other in physics.

The object of the present note is to direct attention again to this proposal of Waidner and Burgess, but from a slightly different standpoint. Instead of making the amount of light emitted under these conditions the unit, it is suggested that it be used as a *fixed point* in a luminosity scale, preferably that scale whose unit is the watt of luminous flux. All of the peculiar advantages of platinum in this connection—its high melting point; its freedom from oxidation and its consequent definiteness of melting point; the purity with which it may be prepared—are really arguments for its use as a fixed point. They are so interpreted in thermometry. There is no more reason why the light from melting platinum should be taken as a unit than there is for calling the melting point of platinum the zero of the temperature scale.

Apart from those advantages of platinum in this connection, which have been very fully set forth in the past, attention will now be called to three points which have not been heretofore emphasized. These appear to the writer to call for careful study of this method of fixing the platinum point on the photometric scale, as perhaps the most practical and promising means now at our disposal for fixing the unit of luminous intensity.

These points are, first, that the amount of luminous radiation from a black body can be accurately calculated by the use of constants whose values are, or soon will be, established with the highest accuracy; second, that the color of the black body at this temperature is that of the present standards; third, that the method of constructing a black body by using wedges of thin metal promises to make this proposal more generally feasible than it was at the time of its original publication.

In regard to the first point, it has been shown[1] that the luminosity of the black body can be calculated from the expression

$$b = \frac{\sigma K^4}{m\pi}\left[\frac{\int_0^\infty J_\lambda L_\lambda d\lambda}{\int_0^\infty J_\lambda d\lambda}\right].$$

[1] Ives and Kingsbury, "The Mechanical Equivalent of Light as Obtained from the Brightness of the Black Body," PHYS. REV., 1916.

where K is the absolute temperature, σ is the constant of the Stefan-Boltzman law, L_λ is the luminosity of the equal energy spectrum, J_λ the rate of energy emission, b the brightness, and m is the mechanical equivalent of light, *i. e.*, the constant necessary to transform the light watts into whatever practical unit is used. (If the light watt is used, m = unity.)

An expression for L_λ has been worked out by Kingsbury;[1] for J_λ is of course to be used the Wien-Planck equation (unless some superior formula is discovered) with the experimental values for the constants σ and c_2. While as shown in a previous paper,[4] the values of these constants, of the mechanical equivalent of light, and the melting point of platinum, are not now sufficiently certain to make this calculation exact, they are all the subject of study by numerous physicists from various points of attack, and will undoubtedly shortly attain the desired definiteness.

Recent experimental work[4] on platinum wedges melted electrically gave for result that if for σ be taken 5.65×10^{-12}; for c_2, 14,390; for K, 2028°; then a value for m of .00139 gives the true value of b in the above equation.

In regard to the second point, it is only an accident, but a very happy one, that the color of the black body at the melting temperature of platinum is almost exactly that of those "4-watt" carbon lamps which now serve as the custodians of the unit of luminous intensity. The practical importance of this is very great. It means that all laboratories can establish the value of the platinum point, in terms of the present unit, without any question arising about their colored light photometric scale. With this point once fixed, every incandescent lamp standard in the world could be destroyed with the assurance that the unit could be accurately reproduced—an assurance which is lacking now when the only "primary" standards are flames considerably different in color from the incandescent lamps best fitted to preserve the unit.

In regard to the third point, the suggestion of Professor Mendenhall,[2] to make experimental black bodies of thin metal wedges of narrow angle to be heated electrically, though made with special reference to pyrometry, is equally applicable to photometry, and suggests that the fixed point in question can be determined with comparatively simple apparatus at not prohibitive expense. Our experimental work on this method, described in a previous paper,[4] appears to show that photometric readings at the melting point of the wedge can be obtained of great definiteness and consistency. (The extreme range in our four meltings was .5 per cent.)

[1] E. F. Kingsbury, "A Luminosity Curve Equation and its Use," PHYS. REV., Feb., 1916, p. 161.

[2] C. E. Mendenhall, "Emissive Power of Wedge-shaped Cavities and their Use in Temperature Measurements," Astrophysical Journal, 33, pp. 91–97, March, 1911.

While the number of melts made by us was perhaps not sufficient to warrant sweeping conclusions, and certain improvements in the apparatus are now obvious, we believe the method to be of such great promise as to warrant its recommendation to the Bureau of Standards as worthy of serious study. Certain details needing investigation are, for instance, the effect if any of the length, breadth and thickness of the platinum strip on the melting point; the best means for removing all tension from the strip; whether the melting point is different for quick or slow heating; the relative and absolute lengths of wedge and aperture to insure the latter being uniformly bright at the instant melting occurs. These are all points offering no apparent difficulties, and while it is probable that the method would be largely independent of variations in these factors, their exact determination would not make the specification of the standard unduly complicated.

In conclusion, the writer would point out that while the suggestions of this paper amount to little more than a bringing together of proposals and ideas which have been published and discussed before, he believes the resultant proposed method of establishing a fixed point in the photometric scale has quite peculiar merit.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
January 19, 1916.

THE RADIANT LUMINOUS EFFICIENCY OF THE CARBON INCANDESCENT LAMP AND THE MECHANICAL EQUIVALENT OF LIGHT.

BY HERBERT E. IVES AND E. F. KINGSBURY.

IN several recent papers [1,2] we have described methods for obtaining the mechanical equivalent of light, and have arrived at an experimental value for that constant. According to our work, one lumen is .00159 watt of luminous flux.

Recently Pirani and Miething,[3] Meyer[4] and Langmuir,[5] using in part data of Lummer and Pringsheim[6] and Nernst[7] on black body brightness have arrived at figures 20 to 30 per cent. lower than ours. This discrepancy is far beyond any to be ascribed to known sources of error in our experimental work (we have estimated our figure to be right to within at least two per cent.), so that we have been interested in checking our work by independent experiments. We have already shown[8] that the method of obtaining this constant through black body brightness is not capable of fixing its value exactly in the present state of our knowledge of the black body constants. Our own experiments on the black body were not sufficiently consistent to warrant any definite conclusion as to the value of the mechanical equivalent thus derived. Our most reliable results—at the platinum melting point—appeared however to favor a figure of .00139, somewhat lower than our previous experimental value.

The present note describes a check on the order of magnitude of this constant by a method described before, which is excellent for this purpose

[1] Ives, Coblentz & Kingsbury, "The Mechanical Equivalent of Light," PHYS. REV., April, 1915, p. 269.

[2] Ives and Kingsbury, "Physical Photometry with a Thermopile Artificial Eye," PHYS. REV., Nov., 1915, p. 319.

[3] Pirani and Miething, "Strahlungsenergie, Temperatur und Helligkeit des Schwarzen Körpers," Ver. der Deutschen Physikalischen Ges., 13, 1915, p. 219.

[4] Meyer, "Der Schwarze Körper als Lichtquelle, etc.," Verh. d. D. Phys. Ges., 21, p. 384, 1915.

[5] Langmuir, "Radiation from Tungsten Filaments and the Mechanical Equivalent of Light," Abs. in PHYS. REV., Jan., 1916, p. 152.

[6] Lummer and Pringsheim, Physik. Zeitschrift, 3, 97, 1901–1902.

[7] Nernst, Physik. Zeitschrift, 7, p. 380, 1906.

[8] Ives and Kingsbury, "Mechanical Equivalent of Light as Obtained from the Brightness of the Black Body," PHYS. REV., 1916.

when the discrepancy in question is so large, although not suitable for exact determination of the value.

The method consists in brief in determining the radiant luminous efficiency of a chosen light source, and comparing this with the total luminous efficiency, thereby obtaining the efficiency losses due to conduction, convection, etc. These are then compared with the estimate of these losses as obtained by independent means.

Thus, as has been previously shown,[1] if F is the luminous flux, P the applied power, R the radiant power, L_T the total luminous efficiency, and L_R the radiant luminous efficiency,[9] then

$$\frac{R}{P} = \frac{\frac{F}{P}}{\frac{F}{R}} = \frac{L_T}{L_R}.$$

Now L_T is obtained by multiplying the efficiency as ordinarily expressed in lumens per watt, by the mechanical equivalent of light. It therefore involves directly the chosen value of the constant in question.

L_R is obtainable by measuring the radiation with and without the interposition of a "luminosity curve" template, it being understood of course that the luminosity curve employed is the one used to determine the mechanical equivalent.

The application of this process to the carbon incandescent lamp, whose efficiency losses are approximately known, will be recognized as one element in the published work on the determination of the mechanical equivalent,[1] and on the application of a small correction to the originally found value.[2] These determinations were made, however, as stated, on a high candle power concentrated filament lamp, matched in color with a standard, but which had not itself been measured for efficiency losses. Some question has been raised too in certain quarters as to the validity of part of the experimental work, so that a careful repetition seemed desirable. The work here described differs from the earlier study in the fact that a new regular "32 candle power" oval anchored filament lamp was used, that being the type for which Hyde [10] has given data on leading-in wire losses, this lamp being as well an original standard calibrated by the Electrical Testing Laboratories to be accurately 4.85 watts per mean spherical candle power or 2.59 lumens per watt. The use of this smaller lamp was made possible by the greater sensibility and completeness of the experimental means now at our disposal.

[9] For the symbols and relations here used see Ives "The Establishment of Photometry on a Physical Basis," Jnl. Franklin Institute, Oct., 1915, p. 409.

[10] Hyde, Cady and Worthing, "A Study of the Energy Losses in Electric Incandescent Lamps," Trans. Ill. Eng. Soc., April, 1911, p. 238.

In the experimental work particular attention was paid to the elimination of all possible errors. The "luminous efficiency meter" shown in Fig. 1 consists of a surface thermopile, before which are two tubes, one clear, the other containing the luminosity curve solution. Either of these can be turned into position at will, and they are of such lengths that when the thermopile mounting is pushed to place against either, the optical distance from light source to thermopile is the same. The luminosity curve solution is that described elsewhere,[2] with a protective water tank 2.5 cm. thick. These tanks are made of glass tubing with plane ends fastened on with paraffine, the whole cell being then embedded in plaster of Paris in a close fitting brass container.[11] (The maximum transmission of the two cells together is .57, by which figure the light deflections are divided.) Nickel plated front and cover (not shown in figure) give protection against air drafts and stray radiation.

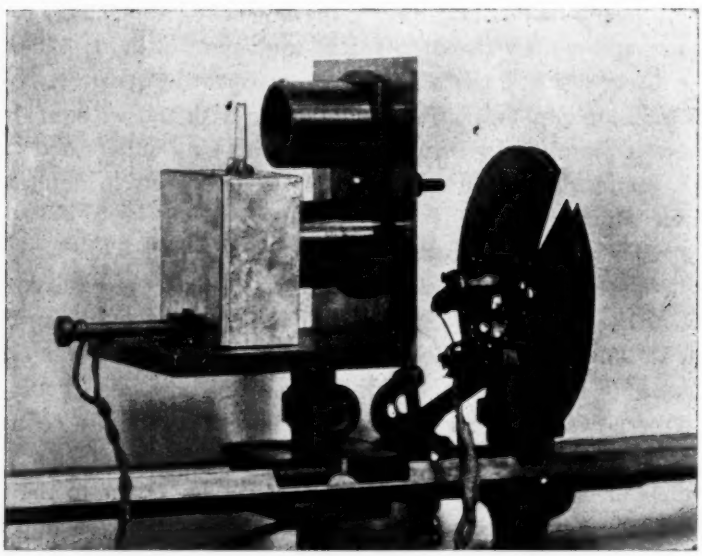

Fig. 1.

Radiant luminous efficiency meter, with cover and screening system removed.

In addition to a very complete screening system (not shown), two somewhat novel features deserve attention—the sector disc employed with the total radiation exposure to keep the total and luminous deflections approximately of the same magnitude, and the shutter. The disc (of

[11] For details of this construction see Ives and Kingsbury, "The Application of Crova's Method of Heterochromatic Photometry to Modern Incandescent Illuminants," Trans. Ill. Eng. Soc., X., No. 8, p. 716, 1915.

aluminum) had a one per cent. opening, and because of the small dimensions of the aperture its edges had to be very carefully bevelled and blackened. It was then calibrated photometrically. Its most important feature, however, was an additional protective disc of tin separated from the acting disc by about five millimeters' air space, and having an opening as small as possible without obscuring the calibrated opening. This cover disc was found necessary because when working with the rather long exposure required by this surface thermopile the disc would warm up enough to appreciably affect the result. The shutter, which was controlled from a distance, was made similarly double-walled.

Some question has been raised as to the thickness of water layer necessary to completely obstruct such infra-red radiation as the copper chloride element of the luminosity curve solution proper transmits. We have previously found two centimeters adequate, with varying thicknesses of water layer, so that the 2.5 cm. used in this arrangement of apparatus was thought ample. In order to test this again we have carried through with great care a number of critical measurements, of which one alone need be described. This was the measurement of the transmission of a 2.5 centimeter water layer, both visually and with the physical photometer comprised by the luminosity curve solution and water tank above described. If this measurement gave different results by the two methods it would indicate an outstanding error due to inadequate water protection. Identical values for this transmission were obtained by the visual method and the physical photometer, showing, as did our other tests, the protection against infra-red to be complete with the 2.5 cm. tank incorporated in the apparatus.

The experimental procedure was the same as that already described in the accounts of these researches,[1, 2] and need not be repeated here.

Our mean value from a long series of readings, for the luminous efficiency of the carbon lamp radiation is

$$L_R = .0045$$

in close agreement with previously obtained values by Karrer[12] and the writers,[1] with slightly different luminosity curve solutions.

Now the total luminous efficiency, L_T, if we use the authors' value for the mechanical equivalent of light, is, for 4.85 w.p.c. or 2.59 lumens per watt,—

$$2.59 \times .00159 = .00412$$

from which the radiation efficiency,

[12] Karrer, "A Method of Obtaining Radiant Luminous Efficiencies, etc.," PHYS. REV., March, 1915, p. 189.

$$\frac{R}{P} = \frac{L_T}{L_R} = \frac{.00412}{.0045} = .915$$

Now the leading-in wire losses as determined by Hyde [10] are from 4–5 per cent. To these must be added convection losses, roughly measured by Drysdale[13] as "not more than 2 or 3 per cent.," and some additional loss (in the direction of measurement) due to the slightly different distribution of radiation by the heated glass bulb from that of the filament, which latter is all that we are concerned with in the "visible" measurement. This loss must be very small, probably not more than 2 per cent. Adding these together $5 + 2 + 2 = 9$, is a not improbable value for the losses, giving 91 per cent. as the radiation efficiency. (If these losses could be accurately determined by other than radiation measurements, a valuable independent method of obtaining the mechanical equivalent of light would be at hand.)

The experimental figure given above is therefore in excellent agreement with independent evidence on the radiation efficiency. If on the other hand we use the value of the mechanical equivalent arrived at by Pirani; .00123,—the radiation efficiency works out at 71 per cent., which is almost out of the question.

We conclude from this that the value .00159 is substantially correct for the mechanical equivalent of light, where light is defined by the luminosity curve, and measured by the photometric method (in agreement with that curve), used by us.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, PA.,
January 19, 1916.

[13] Drysdale, "Luminous Efficiency and the Mechanical Equivalent of Light," Illuminating Engeneer (London), Vol. I, p. 640, 1908.

CHANGE OF RESISTANCE WITH TEMPERATURE OF VARIOUS SODIUM AMALGAMS.

BY RALPH C. RODGERS.

HISTORICAL.

IN the present investigation of the change of resistance of several sodium amalgams with temperature a direct method of measuring the resistance change of the specimen was used by employing the Kelvin double bridge.[1]

A great deal of work has been done on the resistance of mercury and of sodium by various investigators. Among those who have studied the resistance of these metals may be mentioned Matthiessen,[2] Dewar and Fleming,[3] Bernini,[4] Onnes and Clay,[5] Guntz and Broniewski,[6] Onnes,[7] Baltruszajtis,[8] Onnes and Holst,[9] Lohr,[10] Hachspill,[11] Hornbeck,[12] and Northrup.[13]

While various properties of the sodium amalgams have been studied by several investigators including Berthelot,[14] Guntz and Ferée,[15] Kerp and Böttger,[16] Maey,[17] Kurnakow,[18] Schüller,[19] and Vanstone;[20] very

[1] W. Thomson, Phil. Mag., No. 24, 1862, p. 149. Leeds and Northrup, Standard Resistances, Pamphlet No. 4.

[2] Matthiessen, Fortschritte der Physik, Vol. 12, 1856, pp. 452–454; Vol. 14, 1858, pp. 444–445; Phil. Mag., 4th Series, Vol. 12, 1856, p. 199; Vol. 13, 1857, pp. 81–90; Proc. Roy. Soc., Vol. 9, 1857, p. 95–100.

[3] Dewar and Fleming, Proc. Roy. Soc., Vol. 60, p. 76.

[4] Bernini, N. Cimento, Vol. 49, 1903, p. 21.

[5] Onnes and Clay, Communications from Phys. Lab., Univ. of Leiden, No. 99c.

[6] Guntz and Broniewski, Comptes Rendus, No. 26, December, 1908, pp. 1474–1477.

[7] Onnes, K. A. W. Amsterdam, Proc. 14, pp. 818–821, February 22, 1912.

[8] Baltruszajtis, Acad. Sci. Cracovie Bull., 9a, pp. 888–898.

[9] Onnes and Holst, K. A. W. Amsterdam, Proc. 17, pp. 508–513, 1914.

[10] Lohr, Science Abstracts, Vol. 8, Abs. No. 587, p. 192.

[11] Hachspill, Ann. Chim. Phys., 28, Ser. 8, pp. 613–696, 1913.

[12] Hornbeck, PHYS. REV., Series 2, pp. 217–240, September, 1913.

[13] Northrup, Amer. Electrochem. Soc. Trans., 20, pp. 185–203.

[14] Berthelot, Ann. Chim. Phys., 1879, Vol. 18, p. 442.

[15] Guntz and Ferée, Comptes Rendus, 1900, Vol. 131, p. 182.

[16] Kerp and Böttger, Zeit. Anorg. Chem., 1901, Vol. 25, p. 1.

[17] Maey, Zeit. Phys. Chem., 1899, Vol. 29, p. 119.

[18] Kurnakow, Zeit. Anorg. Chem., 1900, Vol. 23, p. 434.

[19] Schüller, Zeit. Anorg. Chem., 1904, Vol. 40, p. 385.

[20] Vanstone, The Chemical News, Vol. 103, No. 2682, p. 181; No. 2683, p. 198; No. 2684, p. 207.

little work has been done on the resistance of the amalgams. Bornemann and Müller,[21] Bornemann and Rauschenplat,[22] and Vanstone[23] have determined the electrical conductivity at fixed temperatures above 0° C.

OBJECT.

The purpose of the present investigation was to determine the change of resistance of several sodium amalgams with change of temperature from − 185° C. to + 150° C., and to study the depression of the freezing-point of mercury in amalgams of small atomic percentage by the method of the sudden change of resistance of the amalgam due to the change to the solid state. Eight specimens of amalgams were studied by the comparison of their resistance change to that of mercury in the same container throughout the range of temperature.

APPARATUS.

The apparatus used consisted of a container to hold the amalgam, a copper resistance thermometer, a Kelvin bridge to determine the re-

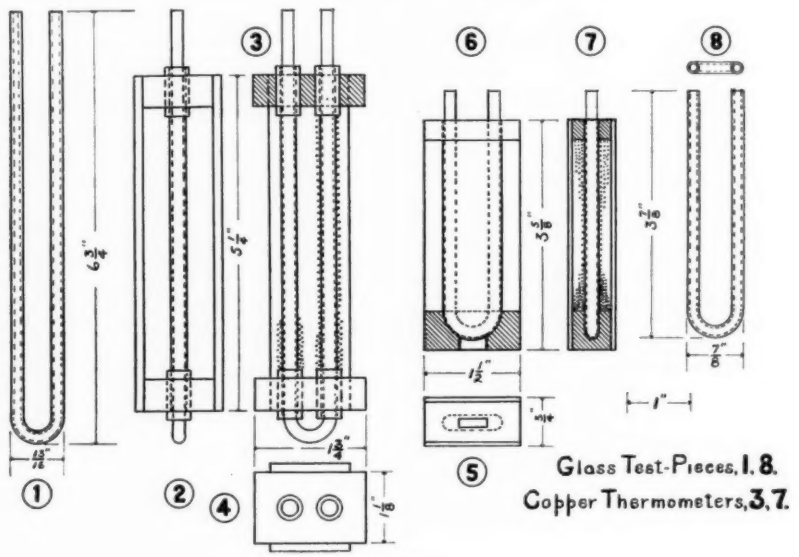

Fig. 1.

sistance of the specimen of amalgam, a Wheatstone bridge to determine the resistance of the copper thermometer.

Various materials were used to make the test-piece to contain the

[21] Bornemann and Müller, Metallurgie, 1910, 7, pp. 396–402.

[22] Bornemann and Rauschenplat, Metallurgie, 1912, 9, pp. 473–486, 505–515.

[23] Vanstone, The Chemical News, Vol. 108, No. 2810, p. 164.

amalgam, such as paper fibre tubing, quartz tubing, and glass tubing. The final test-piece that was used, was made of U-shaped glass tubing, so fashioned as to slip into the copper thermometer as shown in (1) and (3) of Fig. 1. A piece of glass tubing about 40 cm. in length, an average inner diameter of 2.87 mm. was used, this test-piece contained 29.714 grams of pure mercury at 18° C.; the approximate length of the inner bore was about 33 cm. Later, in the work, it was thought best to make a smaller container for the specimen of the amalgam. A piece of glass tubing about 20 cm. in length, an average inner diameter of 3.05 mm. was used. This test-piece contained 19.98 grams of pure mercury at 18° C.; the approximate length of the inner bore was about 17 cm., as shown in (6) and (8) of Fig. 1.

These two test-pieces were calibrated throughout the range of temperature with the change of resistance of pure mercury. Care was taken each time to have the same amount of material by volume in the test-piece and the same conditions were maintained during each of the several runs.

The Copper Thermometers.

The different temperatures of the test-piece were measured by means of a copper thermometer, No. 1. On a thin copper tube of internal diameter of 6 mm. and length of 12 cm. were wound several layers of No. 36 single silk covered copper wire through the length of 8 cm. There was made a duplicate of the same, each having a resistance of about 44.21 ohms at room temperature of 21.5° C. These tubes were mounted in fibre supports as shown in (2), (3) and (4) of Fig. 1, and the ends were soldered together, giving a resistance of about 88.41 ohms at room temperature. To the other ends of the copper wire were soldered three leads, two to one end and one to the other, each lead of a length of 300 cm. These leads were made of No. 24 cotton covered wire and each had a resistance of 0.255 ohm at 20° C.

A smaller copper thermometer, No. 2, was made later by using several layers of No. 30 cotton covered wire which was wound on a form of thin sheet copper as shown in (5), (6) and (7) of Fig. 1. The resistance of this thermometer including its lead wires in melting snow was 33.55 ohms. The lead wires were three in number, connected as in the previous thermometer No. 1, made of No. 20 cotton covered wire, and each lead has a resistance of 0.145 ohm at 20° C.

The resistance of each thermometer was measured by a Wheatstone bridge, a special dial type made by Leeds and Northrup Co. The ratio coils of this bridge were 10 to 1,000, and a check of the bridge was made by a comparison with a Wolff standard resistance of ten ohms, and one of one ohm.

As shown in the diagram of this bridge, Fig. 2, the resistance of the three lead wires, AC_1, CC_1, and BB_1, become a part of the bridge itself; it follows that these lead wires can be considered eliminated by the bridge and any error in them, regarding resistance change, can be neglected.

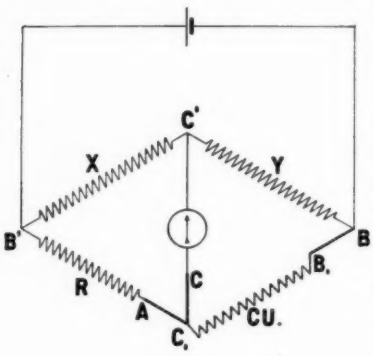

Fig. 2.

Various fixed points were determined carefully on both thermometers, by means of comparison with a standard thermo-junction, calibrated by the Bureau of Standards, at different temperatures. The equation for each thermometer was determined and was of the form $y=mx+b$.

Copper Thermometer No. 1.—The resistance of this thermometer at the ice-point was 81 ohms, and the following equation was used.

$$R_t = 81 + 0.3463t.$$

A change of resistance in the thermometer of one tenth ohm was equal to a change in temperature of 0.28 of a Centigrade degree.

Copper Thermometer No. 2.—The resistance of this thermometer at the ice-point was 33.55 ohms, and the following equation was used.

$$R_t = 33.55 + 0.1468t.$$

A change of resistance in the thermometer of one tenth ohm was equal to a change in temperature of 0.68 of a Centigrade degree.

From the observed data, the following curves were plotted for Thermometer No. 1 and Thermometer No. 2, as shown in Fig. 3.

ARRANGEMENT OF APPARATUS.

The change of resistance of the specimen in the test-piece was measured directly by the Kelvin bridge. From the potential points on the bridge potential lead wires of equal resistance were carried to the specimen in the test-piece. The fall of potential in the specimen of amalgam was balanced by a like fall of potential in the standard low resistance of the bridge.

METHOD OF OBSERVATIONS.

The test-piece, containing the specimen, having been properly connected with the current and potential lead wires to the Kelvin bridge, was immersed in a bath of petroleum ether in its copper container, the petroleum ether was constantly stirred by means of a jet of compressed air. The copper container was then placed in a large Dewar bulb con-

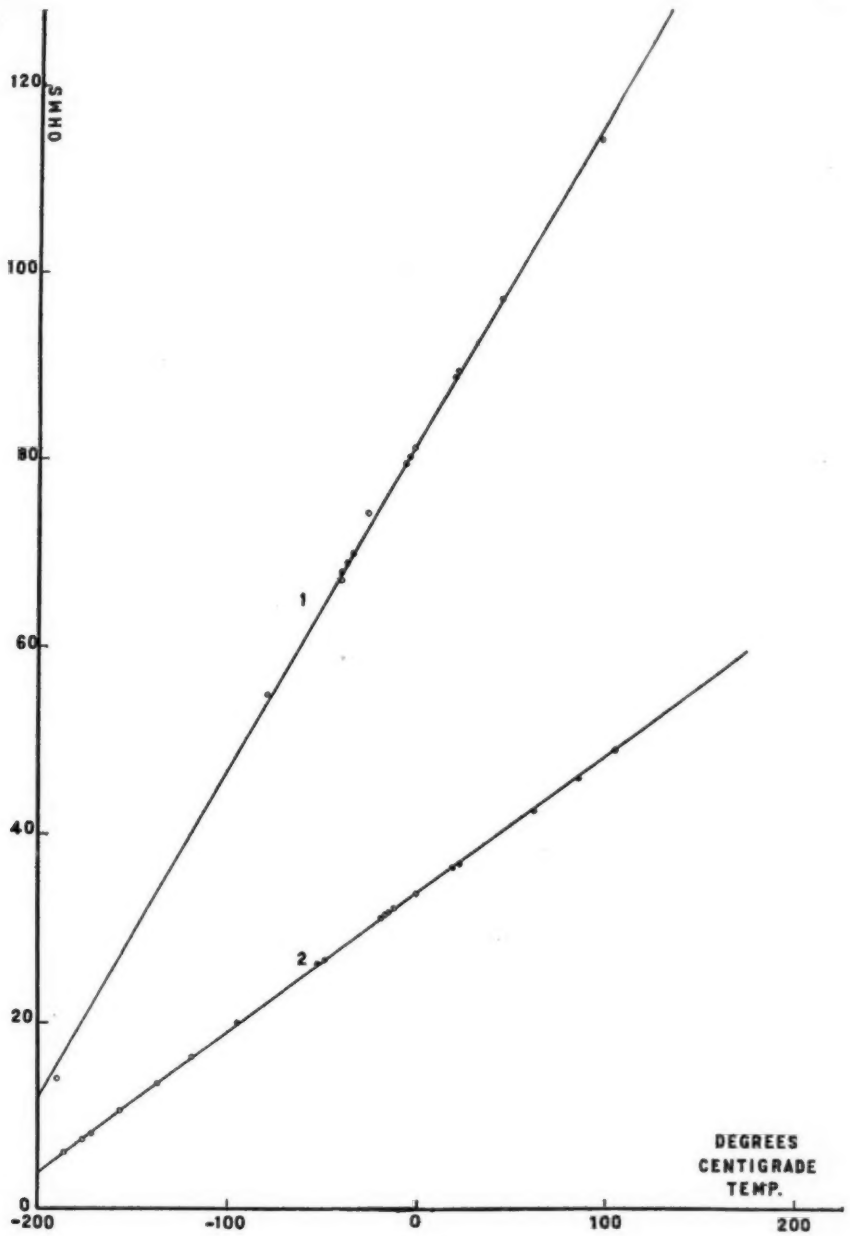

Fig. 3.

taining liquid air, and was gradually cooled to the low temperatures desired. When higher temperatures than room temperature were desired, the test-piece was immersed in a bath of petroleum oil free from any

moisture, and heat was supplied by means of a current passing through a resistance coil wound around the copper container, the apparatus being placed in a Dewar bulb.

Referring to Fig. 4, *A* represents the Dewar bulb; *B*, the space for liquid air; *C*, the copper container filled with petroleum ether; *D*, the copper thermometer; *E*, the holder for the potential and current lead wires for the specimen; and *S*, the air stirrer immersed in petroleum ether.

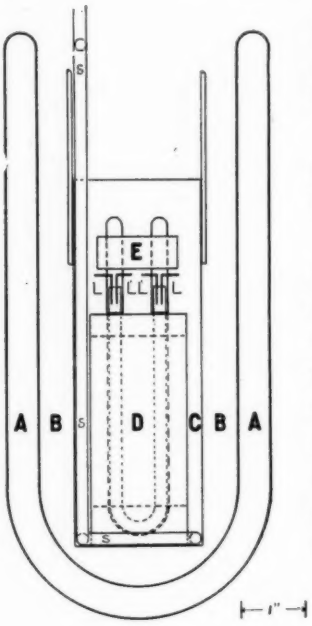

Fig. 4.

The rate of cooling was slow and the temperature of the petroleum ether was assumed to be the same throughout its mass.

Readings were made on the Kelvin bridge at the same time the thermometer bridge indicated its balance. Readings of the resistance of the specimen were made by steps of one half ohm on the copper thermometer, and through the critical points, readings were made every one twentieth ohm, the rate of cooling or warming was very slow. By this means very little temperature lag, if any, was noticed.

THE AMALGAMS OF SODIUM.

Redistilled mercury and pure sodium furnished by Eimer and Amend were used in the preparation of the amalgams. Some paraffin wax was melted and freed from any moisture content; under it was placed a certain amount of pure mercury; by weight a certain amount from clean sodium was gradually added, the action was hastened by heating the whole mass in an evaporating dish. The amalgams were then poured into the cold petroleum ether, which dissolved the paraffin; later each amalgam was placed in separate containers and covered with petroleum ether until used.

METHOD OF ANALYSIS OF THE AMALGAMS.

The amalgams were analyzed by the titration method of the neutralization of a normal solution of hydrochloric acid by a normal solution of sodium hydroxide, phenophthalein was used as an indicator.

RESULTS.

In Figs. 5 to 14, the results of the investigation are shown graphically. In Figs. 5 to 11, the values of the resistance of the amalgam, as ordinates,

are plotted against the resistance of the copper thermometer and also directly in Centigrade degrees, as abscissæ. The temperature of the copper thermometer is expressed in ohms as well as in Centigrade degrees.

The freezing point of each amalgam is obtained from these curves thus plotted. It is assumed that freezing begins at the break of the curve in the liquid state and ends at the break of the curve in the solid state. The semi-frozen state is represented by that part of the curve approximately parallel to the ordinate axis. By taking the average of these points of temperature at the beginning and ending of this part of the curve, the average freezing point of the mercury in the particular amalgam

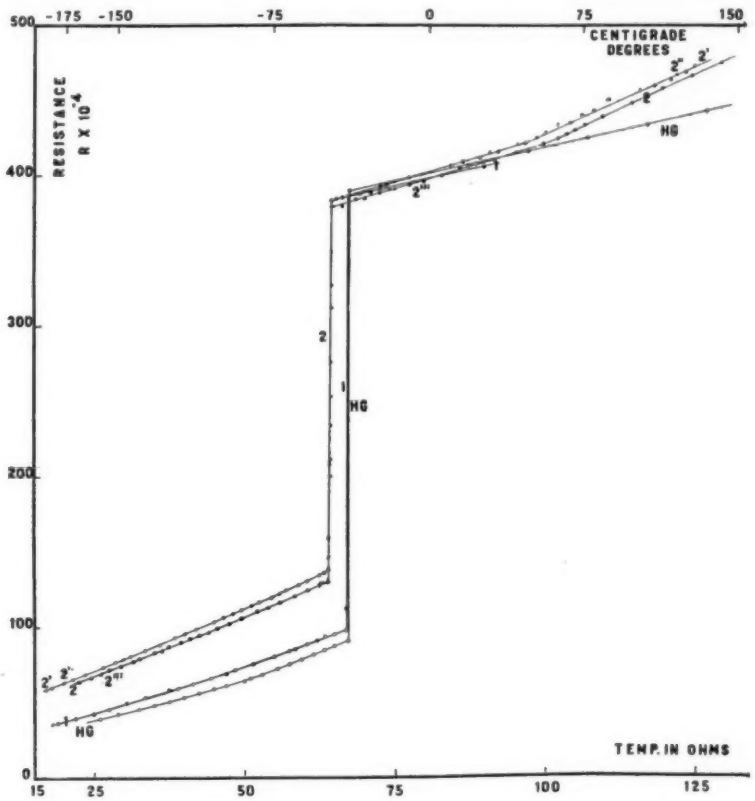

Fig. 5.

is found. These freezing points thus obtained are used in the plotted results as shown in Figs. 12 and 13.

In Fig. 5, the curve marked *HG* is the calibration curve of the glass test-piece by the resistance change of mercury throughout the temperature change. Curve 1 is for amalgam of sodium, showing a trace of

sodium by analysis. Curves 2, 2′, 2″, and 2‴ of an amalgam of sodium, showing by analysis 0.658 per cent. sodium by weight, or an atomic per cent. of 5.452.

In the following discussion of the curves, each amalgam is numbered, the subscripts denote the number of heating runs above the room temperature of 20° C., the superscripts denote the number of cooling runs below the room temperature. Throughout the discussion the room temperature mentioned refers to 20° C.

Two runs were made on amalgam No. 1 for temperature resistance change from room temperature to that of liquid air; the second run being

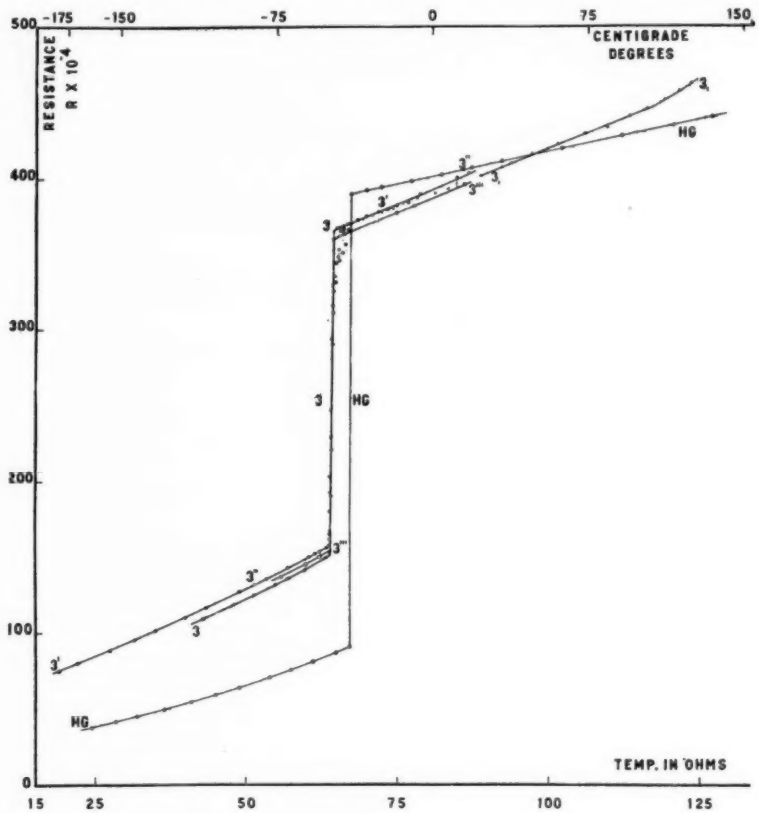

Fig. 6.

a good check on the first run, as shown by the curve passing through the black circles and the black dots. The resistance of amalgam No. 1 being less than the liquid mercury, and greater than the solid mercury throughout the corresponding temperature changes.

Four runs were made on amalgam No. 2, all of them showing points

on the freezing part of the curve, from the liquid to the solid state. Curves 2 and 2‴ check throughout the range of temperature change, and the same is true of curves 2′ and 2″, which, however, show a slight displacement above curves 2 and 2‴; this may be explained because of the nature of the amalgam, which was liquid at room temperature, probably crystals of the compound $NaHg_4$, long prismatic needles in shape, in the excess of mercury. There is a possibility of different arrangement of these crystals on freezing or melting of the sodium amalgam.

The same glass test-piece was used as the container for amalgam No. 3

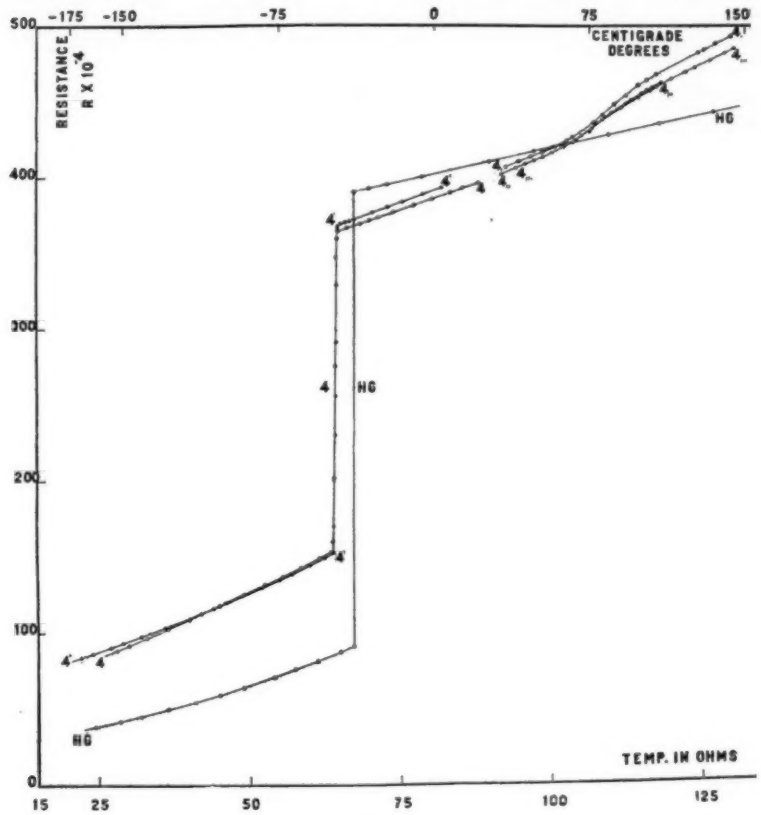

Fig. 7.

as was used in the previous runs. Analysis by weight showing 0.846 per cent. of sodium, the atomic per cent. of 6.93 of sodium, and long prismatic needles in liquid mercury at 20° C.

Four runs were made on the temperature resistance change below room temperature, and one run above room temperature. The curves for the amalgam No. 3 through the change of state coincide, and are of

the same general slope throughout the range of temperature change. The increase in percentage of sodium lowers the freezing point of the amalgam. The resistance of the solid amalgam No. 3 is greater than the resistance of the solid amalgam No. 2, as can be observed from a careful comparison of the two curves, Figs. 5 and 6. These curves give the freezing point of amalgam No. 1 to be − 40.5° C., for amalgam No. 2 to be − 47.93° C., amalgam No. 3 to be − 48.64° C., the freezing point of pure mercury to be −38.80° C.

The same glass test-piece was used as the container for amalgam No. 4 as was used in previous runs. Analysis by weight showing 1.174 per cent. sodium, the atomic per cent. of 9.387, and prismatic needles in a

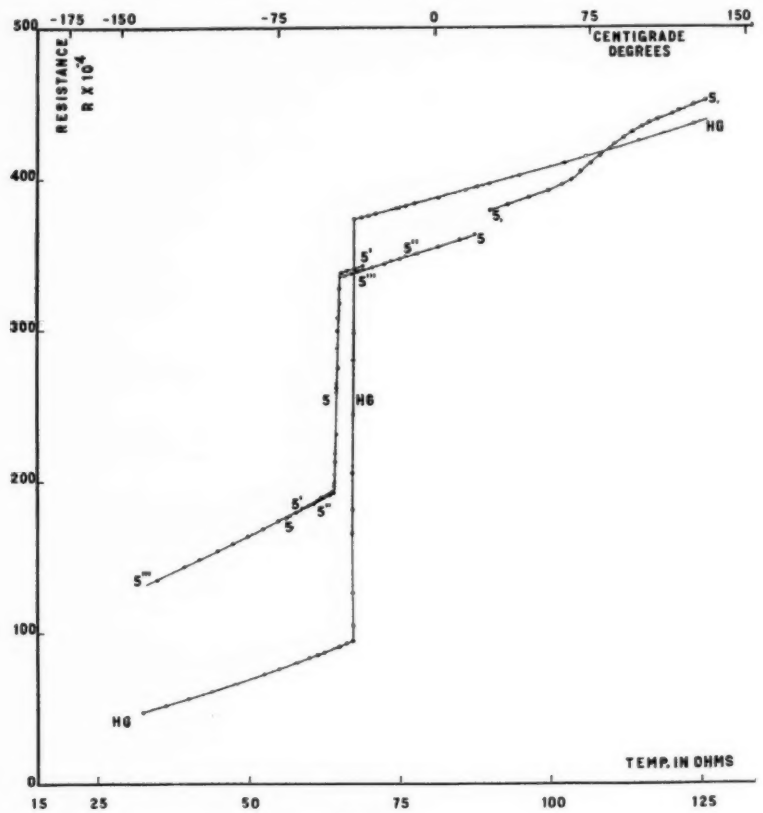

Fig. 8.

semi-pasty mass of the amalgam at 20° C. The freezing point being − 48.43° C.

Two runs were made on the temperature resistance change below room temperature and three runs for temperatures above, the plotted results

being shown in Fig. 7. The curves for cooling runs coincide through the change of state, and show a higher resistance in the solid state for amalgam No. 4 than for amalgam No. 3, a lower resistance in the semi-pasty state than for amalgam No. 3.

The three runs made on the heating of the amalgam above room temperature all show a decided change in the slope of the curves in the neighborhood of the melting point of sodium, 97.5° C., and it is possible that this change may be accounted for by the melting of the prismatic crystals in the amalgam.

A new glass test-piece of the same size was made to use as a container for amalgam No. 5, and was calibrated with mercury in the manner already described. The analysis of amalgam No. 5 shows 1.560 per cent.

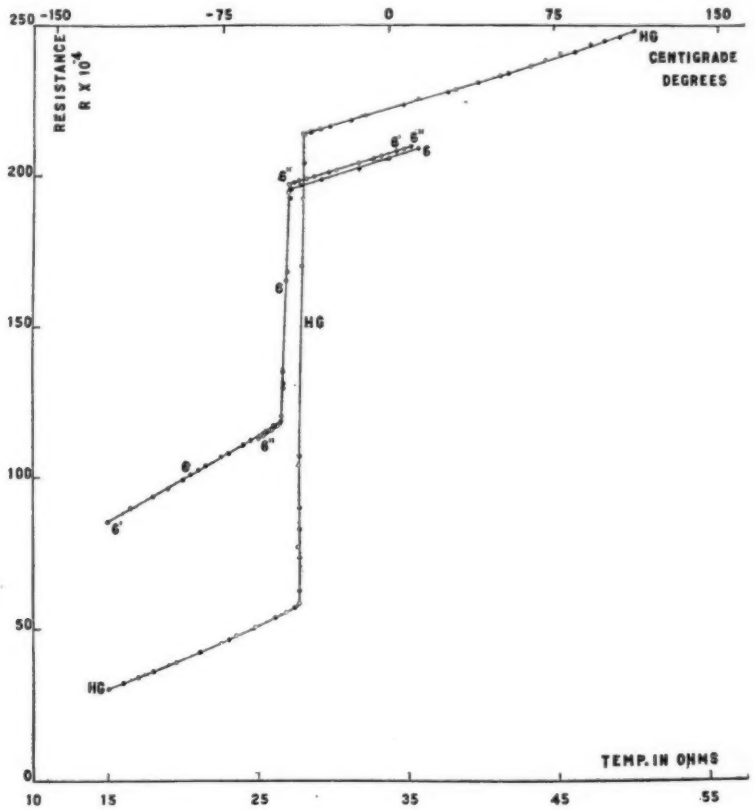

Fig. 9.

sodium by weight, or atomic per cent. of 12.11; prismatic needle crystals in semi-pasty mass of the amalgam at 20° C., freezing point of the amalgam being − 47.85° C.

Four runs were made on the temperature resistance change below room temperature and one above; the plotted results are shown in Fig. 8. The curves for cooling runs coincide throughout the change of state, the amalgam No. 5 shows a higher resistance in the solid state than for amalgam No. 4, a lower resistance in the semi-pasty state than for amalgam No. 4. There is the characteristic displacement of these curves; however, the slopes are the same, as already mentioned in the previous discussion of the other amalgams. The curve for the heating run shows a decided

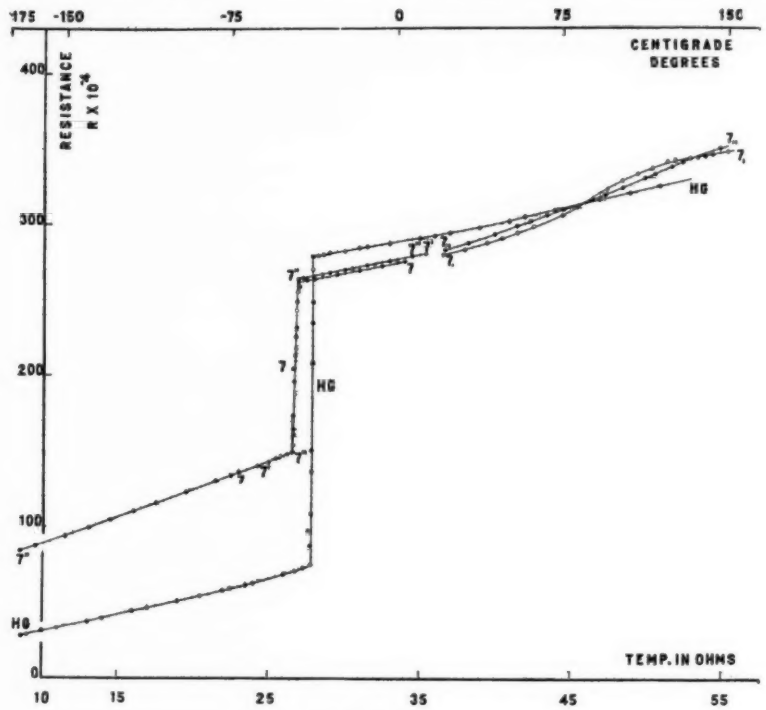

Fig. 10.

bend in the neighborhood of the melting point of sodium similar to the set of curves in the previous Figs. 5, 6, and 7.

These curves already discussed were plotted from carefully inspected data, under the best conditions of a run; plenty of time was taken during the freezing of the amalgams, a great number of readings were made, and a few of these readings are shown as points on the different curves; especially during the change of state most of the points observed, were plotted.

A smaller glass test-piece for the amalgam and a new copper thermometer, more compact in size and shape as shown in Fig. 1, was now used,

with the hope that better results could be obtained. This test-piece was carefully calibrated by two runs with pure mercury throughout the range of temperature change in the same manner as already mentioned.

The analysis of amalgam No. 6 shows 2.10 per cent. sodium by weight, or atomic per cent. of 15.59; prismatic needle crystals in a soft-pasty mass of the amalgam at 20° C., freezing point of the amalgam being − 47.52° C.

Three runs were made on the temperature resistance change below room temperature, and then the glass test-piece was broken. Points on

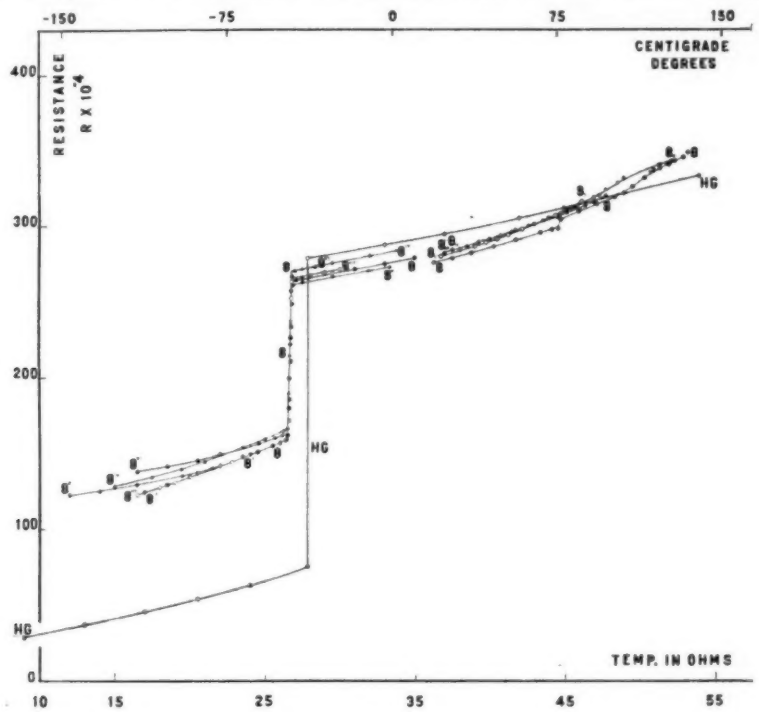

Fig. 11.

all three curves coincide through the change of state, the slopes of the three curves are the same in the soft-pasty state, and the curves show a slight displacement, which is possibly due to the arrangement of the crystals in the amalgam. The plotted results of these runs are shown in Fig. 9.

A new glass test-piece was made and used as a container for amalgam No. 7, which is the same as amalgam No. 6 by analysis.

Three runs were made on the temperature resistance change below room temperature, and two runs were made above, the plotted results are shown in Fig. 10.

Points on all three curves coincide through the change of state, the slopes of the three curves are the same in the soft-pasty state, and again the curves show a slight displacement, as already discussed in previous curves. The two curves for the heating run above room temperature are of the same general shape; there is again evidence of the decided bend in the neighborhood of the melting point of sodium.

TABLE I.

Cooling Run on Amalgam No. 8, Below Room Temperature.

Resistance in Ohms, Copper Therm.	Resistance in Ohms, Amalgam No. 8.	Remarks.
35.00	0.027830	3:45 P.M.
33.00	0.027465	
31.00	0.027100	
30.00	0.026960	Semi-solid state
28.90	0.026825	
28.00	0.026630	
27.50	0.026560	
27.00	0.026450	
26.90	0.026150	
26.80	0.025150	
26.70	0.022650	
26.60	0.018000	Amalgam freezing
26.50	0.016200	
26.40	0.016050	
26.30	0.015900	
26.20	0.015860	
26.10	0.015800	Solid state
26.00	0.015740	
25.50	0.015500	5.35 P.M.

Part of a Cooling Run for Amalgam No. 8, from Room Temperature through the Change of State.

The same glass test-piece was used as a container for amalgam No. 8 as for amalgam No. 7. The analysis of amalgam No. 8 shows 2.67 per cent. sodium by weight, or atomic per cent. of 19.30; prismatic needle crystals in a semi-solid mass at 20° C. Freezing point of the amalgam being − 47.25° C.

Seven runs were made on the temperature resistance change below room temperature, and four runs were made above, the plotted results are shown in Fig. 11.

Points on all seven curves coincide through the change of state, and these curves are in good agreement below the freezing point to the temperature of liquid air. Curves 8^{V} and 8^{VI} show a more decided curvature

TABLE II.

Heating Run on Amalgam No. 8, Above Room Temperature.

Resistance in Ohms, Copper Therm.	Resistance in Ohms, Amalgam No. 8.	Remarks.
37.00	0.027710	4:00 P.M.
38.00	0.027925	
39.00	0.028215	
40.00	0.028500	
42.00	0.029050	Semi-solid state of amalgam, which
44.00	0.029600	on heating becomes liquid.
44.40	0.029660	
44.60	0.029700	
44.80	0.030300	
45.20	0.030450	
45.60	0.030715	
46.00	0.030840	
47.00	0.031250	
48.00	0.031620	
49.00	0.032150	
50.00	0.032850	
51.40	0.033710	
52.00	0.033950	
53.00	0.034415	6:25 P.M.

Part of a Heating Run for Amalgam No. 8, from Room Temperature to about 135° C.

at the lower temperatures than the others, this is possibly due to the arrangement of the crystals in the amalgam on freezing, or some temperature lag as the petroleum ether became thick and was difficult to thoroughly stir at that region of temperature. These curves also show the displacement which is characteristic of the amalgams already mentioned.

A comparison of Fig. 11 with Fig. 10 shows that the resistance of amalgam No. 8 in the solid state is higher than the resistance of amalgam No. 7 in the solid state; also the resistance of amalgam No. 8 is lower than the resistance of amalgam No. 7 in the semi-solid state between room temperature and the freezing point.

A careful study of the four heating runs above room temperature was made with the hope of determining a definite change in the shape of the curves at the region of the melting point of sodium. These curves all show the bend which is characteristic of the other amalgams, they are more or less displaced, the slopes are slightly different from those in the neighborhood of room temperature. No attempt was made to make a continuous run from liquid air temperature to the high temperatures on account of the length of time involved and the necessary change of the stirring bath of petroleum ether to that of petroleum. Plenty of time

was used, however, the runs were in length from six to eight hours of continuous observations. Care was taken to obtain a slow rate of cooling through the freezing of each amalgam, and then checking runs were made under the same conditions. Throughout the whole investigation care was taken to assure repetitions of the conditions governing the different runs of the several amalgams.

From the data already obtained, a curve was plotted; the melting or freezing points of the amalgams as ordinates and the atomic percentage of sodium in the amalgam as abscissæ.

TABLE III.

Specimen.	Wt. %.		Atomic %.		Melting Pt. Deg. C.	Depression Deg. C.
	Na.	Hg.	Na.	Hg.		
Hg.	0	100	0	100	−38.80	0.00
1	Trace	99.9+	1.05	98.950	−40.50	1.70
2	0.658	99.342	5.452	94.548	−47.93	9.13
3	0.846	99.154	6.930	93.070	−48.64	9.84
4	1.174	98.826	9.387	90.613	−48.43	9.63
5	1.560	98.440	12.110	87.890	−47.85	9.05
6	2.100	97.900	15.590	84.410	−47.52	8.72
8	2.670	97.330	19.306	80.694	−47.25	8.45

Referring to Fig. 12, the curve plotted shows an eutectic point in the region of − 48.75° C., with an atomic per cent. of sodium in the amalgam of 5.90, which is a higher value than that obtained by Vanstone.

TABLE IV.

Specimen.	Atomic Per Cent.		Resistance in Ohms of Specimen.			Per Cent. Change.	Melting Point.
	Na.	Hg.	Liquid.	Solid.	Change.		
Hg.....	0.00	100.00	0.03900	0.00910	0.02990	76.70	−38.80
Amalgam 1....	1.05	98.95	0.03860	0.00982	0.02878	74.50	−40.50
2....	5.452	94.548	0.03830	0.01380	0.02450	63.80	−47.93
3....	6.930	93.070	0.03670	0.01490	0.02180	59.60	−48.64
4....	9.387	90.613	0.03642	0.01542	0.02100	57.70	−48.43
5....	12.110	87.890	0.03375	0.01920	0.01455	43.15	−47.85
6....	15.590	84.410	0.02612	0.01495	0.01117	42.55	−47.52
8....	19.306	80.694	0.02660	0.01665	0.09950	37.40	−47.25

From the data already obtained, Table IV., a curve was plotted; the melting or freezing points of the amalgams as ordinates and the percentage change of resistance of the amalgam on freezing as abscissæ. Referring to Fig. 13, the curve plotted shows a sharp bend in the region of

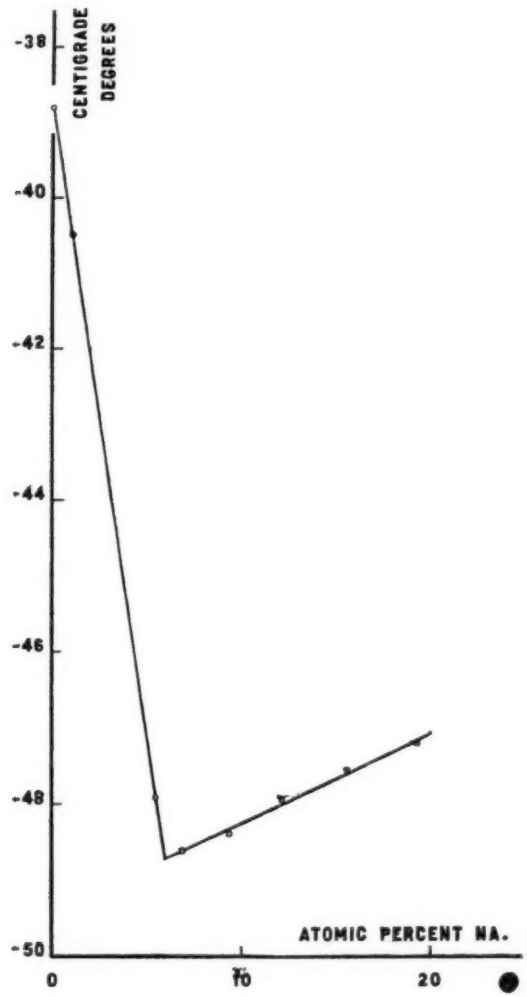

Fig. 12.

$-48.75°$ C., with a percentage change in resistance on freezing of 64.4; it is interesting to note that this sharp bend in the curve coincides with the temperature of the eutectic point of the curve plotted in Fig. 12.

Another curve was plotted from the same data, using as ordinates the atomic percentage of sodium in the amalgam, and as abscissæ, the percentage change of the resistance of the amalgam on freezing.

The results are plotted as shown in Fig. 14; through six of the points a smooth curve can be drawn, the remaining two points probably are in error.

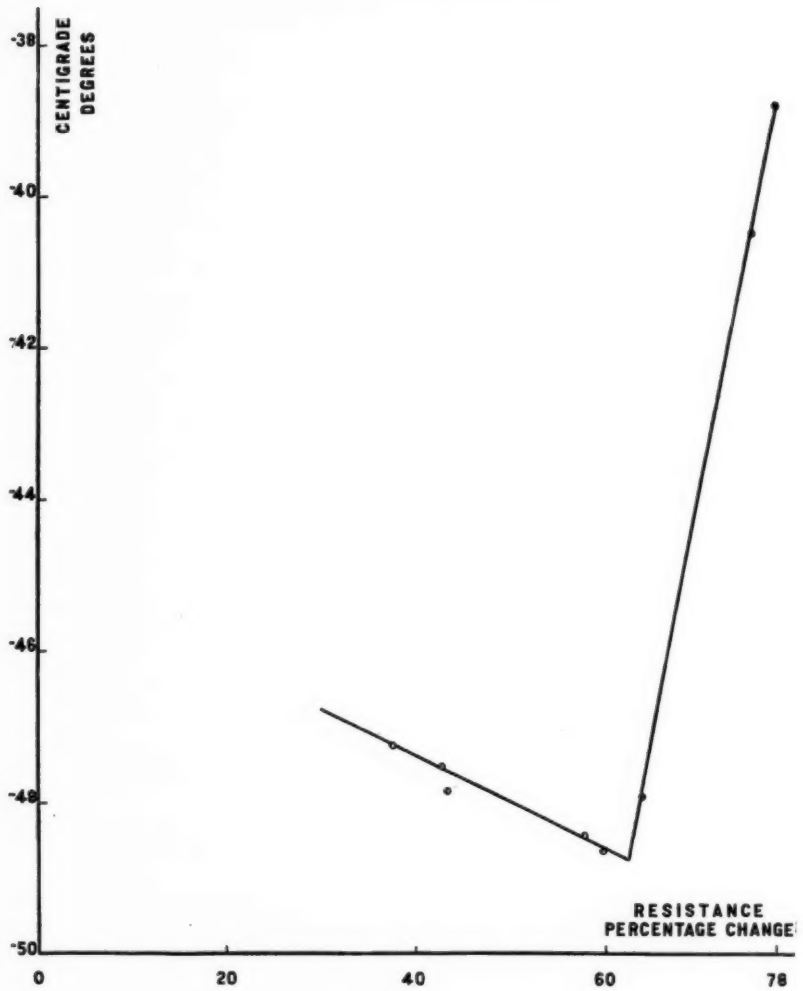

Fig. 13.

The work will be carried on in the near future, using amalgams of higher percentage of sodium.

The author wishes to acknowledge his indebtedness to Prof. E. L. Nichols, at whose suggestion the work was begun, to Prof. J. S. Shearer and Prof. Ernest Blaker who aided and encouraged the work. Valuable assistance has been received from Dr. R. C. Snowdon, Mr. C. C. Murdock and others.

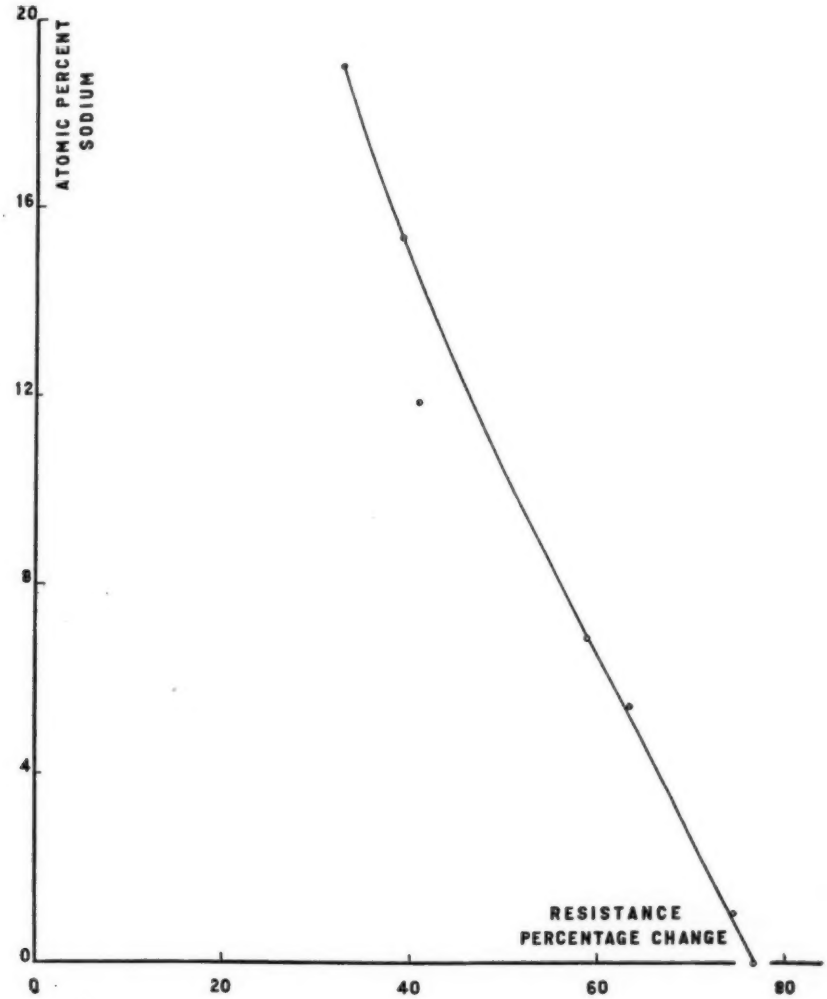

Fig. 14.

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THE LUMINOSITY OF THE POSITIVE COLUMN IN GASES AT LOW PRESSURES.

BY H. A. WILSON.

THE following paper contains an account of a series of experiments on the variation of the light emitted by the positive column with the electric current, gas pressure, temperature, and potential gradient.

It will be convenient to begin by explaining a theory of the light emission which has been found to agree with the results obtained. In the positive column the current is carried by negative electrons and positive ions which are present in nearly equal numbers. The velocity of the electrons is much greater than that of the positive ions so that practically all the current is carried by the electrons. If e denotes the charge on one electron and i the current passing through the positive column the i/e will be the number of electrons passing per second through any cross section of the positive column.

Let us suppose that the emission of any particular spectral line is due to collisions between the electrons and gas molecules but that these collisions do not cause any emission unless the velocity of the electrons is greater than a certain value. Also suppose that the amount of light emitted is proportional to the number of collisions which produce emmission. The number of free paths described by the electrons in one cm. in the positive column per sec. is $i/e\lambda$ where λ denotes the mean free path of the electrons. The number of these greater than a length x is $i\epsilon^{-x/\lambda}/e\lambda$ so that if x is taken equal to the shortest free path, at the end of which the electrons have enough energy to produce emission then the emission should be proportional to $i\epsilon^{-x/\lambda}/e\lambda$.

If the potential gradient in the positive column is denoted by X then x will be inversely proportional to X. Let $x = V/X$ where V is a constant and let $\lambda^{-1} = Cp\ 273\ \theta^{-1}$ where C denotes the number of mean free paths per cm. at one mm. of mercury pressure and 0° C., p denotes the gas pressure and θ the absolute temperature. Then

$$\frac{i\epsilon^{-x/\lambda}}{e\lambda} = \frac{273Cpi}{e\theta}\,\epsilon^{-\frac{VCp273}{X\theta}}.$$

Hence if I denotes the amount of light, of the particular wave-length in

question, emitted by the positive column per sec. we have

$$I = \frac{A273ip}{\theta} \epsilon^{-\frac{VCp273}{X\theta}},$$

where A is a constant. Let t denote the temperature on the Centigrade scale so that $\theta = 273 + t$ and let $f = (273 + t)/273$ so that

$$I = \frac{Api}{f} \epsilon^{-\frac{VCp}{Xf}}.$$

Hence

$$\log_\epsilon \frac{If}{pi} = \log_\epsilon A - \frac{CVp}{Xf}. \qquad (1)$$

According to this equation $\log_\epsilon(If/pi)$ should be a linear function of p/Xf and the slope of the line representing this linear function should be equal to VC. Hence according to this theory we ought to be able to determine VC from measurements of I, p, i, X and t and if we know C we can calculate V.

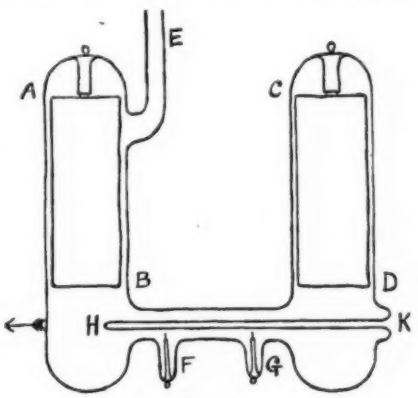

Fig. 1.

The positive column was produced in the vacuum tube shown in Fig. 1. Two glass tubes AB and CD were closed at both ends and joined by a tube BG about one cm. inside diameter and 6 cm. long. At A and C large electrodes of sheet aluminium were fixed inside AB and CD as shown.

The current from a battery of 1,200 small dry cells could be passed through the tube between the large electrodes A and C. In this way a positive column was obtained in the tube BG. At F and G two small electrodes of fine platinum wire were sealed into BG as shown and were connected to an insulated electrostatic voltmeter. The potential difference between F and G divided by the distance between them gave the average potential gradient in the positive column between F and G. A thin-walled glass-tube HK closed at H was sealed on at K as shown so that it lay along the axis of the tube BG. This tube was about one mm. in diameter and a thermo-couple of nickel and iron wires could be inserted into it at K. The junction between the two wires could be moved along the tube HK so that the distribution of temperature along HK could be found. The couple was calibrated by comparison with a mercury in fused quartz thermometer and was found to give an E.M.F. proportional

to the temperature difference up to 250° C. It was found that the temperature was constant between H and G (Fig. 1) and the junction was afterwards kept near F and its temperature was taken to be that of the positive column.

The tube E (Fig. 1) was connected to a Töpler pump, McLeod gauge, phosphorus pentoxide bulb and to an arrangement for introducing different gases into the apparatus.

The intensity of the light emitted by the positive column in BG, in the direction of the arrow at H, was compared with that of the light, of the same wave-length, from a small incandescent electric lamp, by means of a Hilger's spectrophotometer. The current through the small lamp was measured with an accurate ammeter and was kept constant during each series of observations.

The results obtained with helium will be described first. The helium was obtained by heating monazite sand to a dull red heat and was sparked with oxygen over caustic soda solution until no further diminution of volume occurred, the excess of oxygen was removed with phosphorus and the helium then admitted into the apparatus. The helium was further purified by depositing sodium inside a glass tube connected to the apparatus, by electrolysis through the glass, which was heated to enable it to conduct sufficiently. After being purified in this way for about 10 hours the spectrum of the gas, which was at about 10 mm. pressure, showed only helium and mercury lines with a very faint indication of the nitrogen bands. Since the presence of a small amount of nitrogen is sufficient to entirely obscure the spectrum of helium it was concluded that the gas was very nearly pure. The following table contains the results obtained with helium. The yellow line 5876 was used. The light intensity I is given in arbitrary units. p denotes the gas pressure in mms. of mercury; t the temperature in degrees Centigrade, X the potential gradient in volts per cm. and i the current the unit being 5×10^{-3} ampere.

p	t	X	i	I	p/fX	If/pi
9.55	125	19.7	6.1	265.	0.332	6.64
5.65	80	16.7	4.5	250.	0.262	12.65
3.25	75	14.1	4.9	331.	0.182	26.4
1.92	72	12.9	4.73	334.	0.118	46.4
1.12	64	11.2	4.34	265.	0.0814	67.1
0.62	55	9.3	3.6	200.	0.0556	107.5
0.33	34	30.3	0.025	1.22	0.00974	165.0

The values of p/fX and $\log_e If/pi$ are shown graphically in Fig. 2.

The points representing the experimental results fall nearly on the straight line, the slope of which gives $VC = 10$. It appears that the results obtained agree with the theory proposed in a satisfactory way. The result at $p = 0.33$ is especially noteworthy for in this case the current was more than one hundred times smaller than at the other pressures. It was found that at any particular pressure the light intensity was nearly proportional to the current. When the current is increased the temperature in the positive column rises and the potential gradient diminishes but p/fX and If/pi change only slightly.

The results obtained with nitrogen will now be described. The nitrogen was obtained by the decomposition of ammonium nitrite and its spectrum showed only nitrogen and mercury lines. The following table gives some of the results obtained. The wave-length observed was 6015.

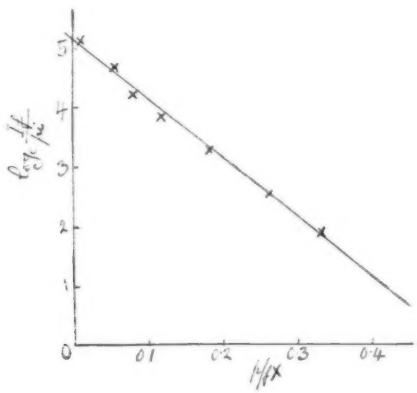

Fig. 2.

p	i	X	i	I	p/fX	If/pi
0.62	79	23.3	1.6	8.55	0.0206	11.1
0.327	59	13.2	1.3	4.11	0.0204	11.8
1.24	154	31.6	3.5	13.6	0.0251	4.9
1.24	107	36.0	1.6	6.5	0.0248	4.6

These results agree with the view that If/pi is approximately a function of p/fX. The following results were also obtained with nitrogen.

p	i	X	i	I	p/fX	If/pi
2.56	188	47.3	3.63	19.5	0.032	3.65
1.38	126	33.8	2.35	11.2	0.0279	5.05
0.74	99	22.4	2.35	11.4	0.0243	8.92
0.396	74	14.7	2.30	9.5	0.0212	13.2
0.21	66	11.4	1.90	5.14	0.0148	16.0
0.099	42	10.1	0.13	0.37	0.0085	33.0

The values of $\log_e If/pi$ and p/fX are shown graphically in Fig. 3. The slope of the straight line gives $CV = 96$. This result was confirmed by a set of experiments in which the temperature was not measured but the relation between X/p and I/pi was found for three values of i proportional to the numbers 1, 2 and 4 respectively. For each value of i a cuvre was drawn representing the relation between I/pi and X/p. The curves were nearly parallel and the curve for the current 4 was twice as far from the curve for the current 2 as the latter was from the curve for current 1. A curve was therefore drawn, on the other side of the current 1 curve, at a

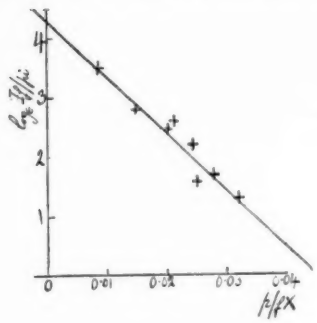

Fig. 3.

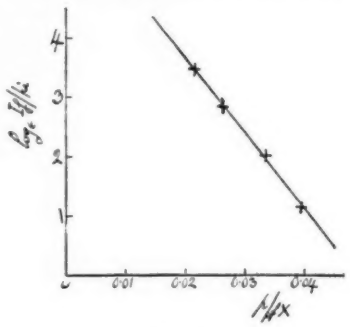

Fig. 4.

distance from it equal to the distance between the current 2 and the current 1 curves and this curve was taken to represent the relation between X/p and I/pi for zero current in which case there would be no rise of temperature. The values of p/X and $\log_e I/pi$ got from the zero current curve when plotted gave a straight line the slope of which gave $CV = 93$ which agrees well with the previous result got by measuring the rise of temperature in each case. This appears to show that the thermocouple gave the temperature of the positive column sufficiently accurately.

The following table gives a set of results obtained with the red line 6562 from hydrogen.

p	t	X	i	I	p/fX	If/pi
2.75	210	39.5	8.3	4.05	0.0393	3.14
1.48	141	29.5	5.55	3.97	0.0330	7.33
0.74	94	21.0	3.75	3.46	0.0261	16.8
0.396	59	15.15	2.30	2.39	0.0214	32.0

The values of $\log_e If/pi$ and p/fX are shown graphically in Fig. 4. The slope of the straight line gives $CV = 130$.

Some observations were also made on the green mercury line obtained

when the vacuum tube was filled with hydrogen containing a small amount of mercury vapor derived from the mercury in the Töpler pump and gauge. The temperature was not observed in this case. The following table contains the results of one series of observations.

p	X	i	I	p/X	I/pi
4.12	61.2	2.6	83.4	0.0673	7.78
4.12	65.1	1.6	55.1	0.0663	8.36
2.66	44.3	2.7	128.	0.060	17.8
1.66	35.3	2.7	147.	0.0471	32.8
1.06	27.5	2.5	161.	0.0386	60.8
0.69	21.9	2.15	161.	0.0315	108.5
0.434	17.6	2.1	150.	0.0246	164.5

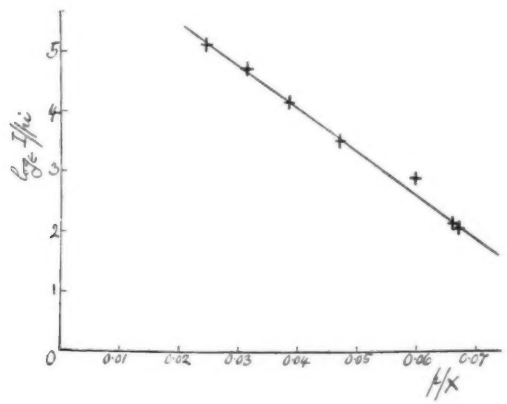

Fig. 5.

The values of p/X and of $\log_e I/pi$ are shown graphically in Fig. 5. The slope of the straight line gives $CV = 72$. This value of CV requires correcting for the rise of temperature. It was found that the red hydrogen line gave a value of CV nearly equal to 72 when the temperature was not allowed for. It follows that the true value of CV, for the green mercury line from mercury in hydrogen, is approximately 130 as for the red hydrogen line.

The values of CV found are collected in the following table.

Gas.	Wave-length.	CV	CV'
Helium	5876	10	34
Nitrogen	6015	96	342
Hydrogen	6562	130	130
Mercury in hydrogen	5461	130	...

The numbers given in the last column headed $C'V'$ are the numbers found by Townsend[1] as the result of experiments on the ionization of gases by collisions with negative electrons. C' denotes the maximum number of new ions produced by one electron while moving one cm. in the gas at one mm. pressure and V' denotes the average potential difference required to give an electron enough energy to ionize a molecule of the gas. In the case of hydrogen CV and $C'V'$ are equal but in nitrogen $C'V'$ is much greater than CV. It appears that an electron can cause a molecule of nitrogen to emit light when the electron's energy is less than the average energy required to ionize the molecule.

In the theory explained at the beginning of this paper it was assumed that the smallest free path, at the end of which a collision would cause emission of light was inversely proportional to the potential gradient. This would follow if the electrons lost all their energy at each collision so that the energy at the end of a free path of length x would be proportional to xX. Franck and Hertz have recently shown that in helium electrons lose very little of their energy when they collide with the molecules unless the collision results in ionization. This is no doubt the explanation of the very small value of CV found in helium. The energy of an electron in helium goes on increasing until it becomes sufficient to produce ionization and the apparent free path is therefore very long so that C is very small.

The mean free path of an electron moving with a high velocity in hydrogen at one mm. pressure is 0.072 cm. This value is calculated from the viscosity of hydrogen taking the free path of an electron to be $4\sqrt{2}$ times that of a molecule in accordance with Maxwell's well known theory. If we take C for hydrogen equal to $(0.072)^{-1}$ we get $V = 9.4$ volts which is rather less than the minimum ionizing potential for hydrogen which according to Franck and Hertz is 11 volts.

The mean free path of an electron in nitrogen is about 0.04 cm. at one mm. pressure which gives $V = 3.8$ volts. The minimum ionizing potential for nitrogen according to Franck and Hertz is 7.5 volts. The values of V do not appear to be related to Planck's quanta of energy for the wave lengths of the spectral lines observed.

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HOUSTON, TEXAS.

[1] Electricity in Gases, p. 295, 1915.

DETERMINATION OF THE LAWS RELATING IONIZATION PRESSURE TO THE CURRENT IN THE CORONA OF CONSTANT POTENTIALS.

BY EARLE H. WARNER.

INTRODUCTION.

THE "corona" is the glow which surrounds conductors when there exist high potential differences between them and neighboring bodies. A careful study of the corona phenomena is necessary (1) to determine the factors which regulate the loss of power due to the corona, which on long transmission lines may be an important item, and (2) to obtain data from which a theory can be developed which will, with mathematical rigor, explain the corona effects. The first of these objects has been quite successfully carried out by Peek, Whitehead, Ryan and others. The only advances toward a theoretical explanation of the corona have been made by Bergen Davis[1] and Townsend.[2] In these two theories the authors have assumed that the corona is an ionization phenomenon. That is, they assume that the high potential difference causes the few ions which are always present in a gas to move with a velocity sufficiently great to break the molecules with which they collide into two parts, one bearing a positive charge and one a negative charge. All these charged particles then move, because of the influence of the field, toward one or the other of the terminals. The presence of these ions thus explains the conductivity of the gas and the acceleration of the ions explains the light effect. If the corona is an ionization phenomenon one would expect, if the corona apparatus was inclosed, at the instant the corona appeared, *i. e.*, at the instant the molecules were broken up into ions, that the pressure in the apparatus would increase; because according to kinetic theory the greater the number of particles in a given volume the greater the pressure. This pressure increase was first discovered by Dr. S. P. Farwell,[3] working in this laboratory. The above mentioned theories assume ionization but do not account for such a pressure increase. Under certain circumstances this pressure increase can amount to as

[1] "Theory of the Corona," Proc. A. I. E. E., January, 1911.

[2] "The Discharge of Electricity from Cylinders and Points," Phil. Mag., May, 1914.

[3] "The Corona Produced by Continuous Potentials," Proc. A. I. E. E., November, 1914.

much as three cm. of mercury. This pressure increase can not be due to the heating effect of the current, because it occurs very quickly and if the current is broken in a few seconds, the pressure at once returns to its initial value. The heating effect of the current becomes noticeable only after several seconds and then when the current is broken the pressure does not at once return to its initial value but it requires some time for the heated gas to cool off. Since the conception of ionization is so intimately associated with the idea of increase in pressure, it seemed important to determine the laws relating this ionization pressure to the corona current.

THEORY.

Dr. J. Kunz has developed a theory which predicts how this pressure increase should vary with the current. One can best understand his development by thinking of the corona as occurring around a wire which is coaxial with a cylinder. See Fig. 1, which represents a cross section

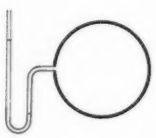

Fig. 1.

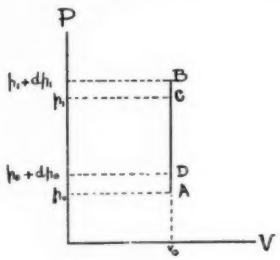

Fig. 2.

of such a corona tube. Suppose the ends of the tube to be closed, so as to inclose a constant volume v_0. When the wire is connected to a very high positive potential and the case grounded the corona glow appears around the wire and the pressure instantly increases from atmospheric to some higher value. Let the condition of the gas at the beginning of the experiment be represented by the point A, on the $p-v$ plane. (See Fig. 2.) The volume is then v_0 and the pressure p_0.

Step I.—Apply a potential difference e between the wire and the case. Some current i will flow and the pressure will immediately jump from p_0 to a higher value, say p_1. The state of the gas will now be represented by the point C. The work done by the current per second, ei, will then be equal to the increase of internal energy of the gas ΔU, plus the work done by the gas W_1, due to the pressure increase. This energy equation gives us

$$ei = \Delta U + W_1. \qquad (1)$$

Step II.—Let us force into the tube a small amount of gas. This

will require work dW_2 and the pressure will increase from p_1 to $p_1 + dp_1$ and can be represented by the state point B. Then

$$dW_2 = -v_0 dp_1. \tag{2}$$

The total work to change the gas from state A to state B has then been

$$ei + dW_2 = \Delta U + W_1 - v_0 dp_1. \tag{3}$$

Now let us start again with the same initial conditions and by two different steps arrive at the same final condition.

Step III.—When the state of the gas is A let us force in a small amount of gas. This will require work dW_3 and the pressure will increase from p_0 to $p_0 + dp_0$, which may be represented by the state point D. Then

$$dW_3 = -v_0 dp_0. \tag{4}$$

In the existing conditions the size of the current depends not only on the potential difference but also upon the initial and final pressures. The increase in current causes an increase in pressure which tends to stop the current. The steady condition of the current represents a condition of equilibrium between the attempt of the current to increase the pressure and the attempt of the increased pressure to stop the current.

Step IV. Now apply the same potential difference e. Let that current i' flow so that it will cause the pressure to increase from $p_0 + dp_0$ to $p_1 + dp_1$, that is, so that the state of the gas can be represented by B. Then as in Step I.

$$ei' = \Delta U' + W_4. \tag{5}$$

In the last two steps the total work required to change the state of the gas from A to B is

$$ei' + dW_3 = \Delta U' + W_4 - v_0 dp_0. \tag{6}$$

Then by the law of the conservation of energy, the work required to change a system from one state to another is independent of the path, we have

$$\Delta U + W_1 - v_0 dp_1 = \Delta U' + W_4 - v_0 dp_0 \tag{7}$$

or

$$\Delta U - \Delta U' + W_1 - W_4 = v_0(dp_1 - dp_0). \tag{8}$$

Subtracting (5) from (1) we have

$$\Delta U - \Delta U' + W_1 - W_4 = e(i - i'). \tag{9}$$

Therefore

$$e(i - i') = v_0(dp_1 - dp_0). \tag{10}$$

But

$$i = i' + di.$$

Then

$$edi = v_0 d(p_1 - p_0) \tag{11}$$

and integrating

$$i = \frac{v_0}{e}(p_1 - p_0) + \text{a constant.} \qquad (12)$$

Since $(p_1 - p_0)$ represents the increase in pressure, that is, the ionization pressure, this equation shows that the ionization pressure should be exactly proportional to the corona current.

It was the object of the experiments which have been performed to test this relationship with pure gases in the tube.

APPARATUS.

The constant potentials were obtained from a battery of continuous current shunt-wound 500-volt generators connected in series.

The corona tube was of the wire and coaxial cylinder type. (See Fig.

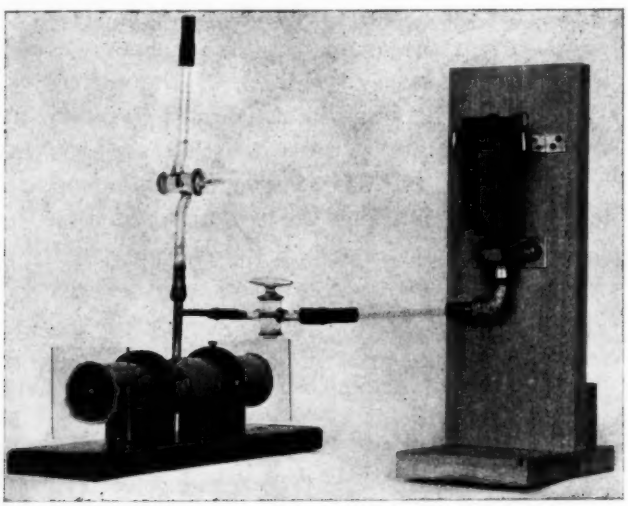

Fig. 3.

3.) Glass plates with holes for the wire to pass through were sealed to the ends of the tube so that the holes were on the axis of the cylinder. The wire, No. 32, copper, passed through the holes and was thus coincident with the axis of the cylinder. The wire was sealed into these holes and held taut by red sealing wax. To the cylinder was soldered a small " T " tube, one side of which was joined to the vacuum pump and the other side was connected to a Bristol aneroid pressure gauge.

The increase in pressure was measured by this Bristol gauge. Any increase in pressure caused it to bend slightly and so rotate the mirror. By observing the deflection of a beam of light over a scale, which had

previously been calibrated by reading simultaneously the deflected beam and a water manometer connected directly to the gauge, the increase in pressure in cm. of water could be determined. The advantage of such a pressure measuring instrument in this experiment is that it is very quick in its action. The instant the pressure increases the gauge jumps right up to its new position and a reading can be taken in a very few seconds. It was necessary to read this pressure increase quickly because if much time was required, the heating effect of the current would increase the pressure also.

The current was measured by a Type *H* D'Arsonval galvanometer. The apparatus was connected as is shown in Fig. 4.

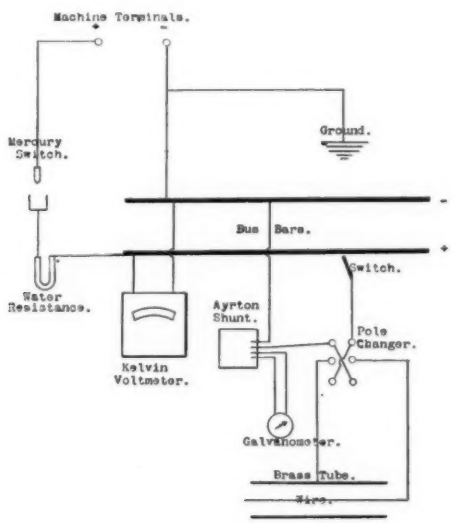

Fig. 4.

DISCUSSION.

Experiments were made when the wire was positive and the case grounded with dry air, hydrogen, nitrogen, carbon dioxide, oxygen and ammonia as the gases in the tube. Considerable care was taken to see that these gases were absolutely pure. They were all dried carefully before they were used. The following curves (Figs. 5, 6, 7, 8, 9) show graphically the results. Fig. 10 shows all the curves plotted to the same scale. With this scale the hydrogen curve should be continued until its ordinate is equal to that of the carbon dioxide curve.

The fact that the points all lie so accurately on a straight line shows conclusively that experiment verifies the prediction made by Dr. Kunz's theory. The law can then be stated that, in the gases studied with the

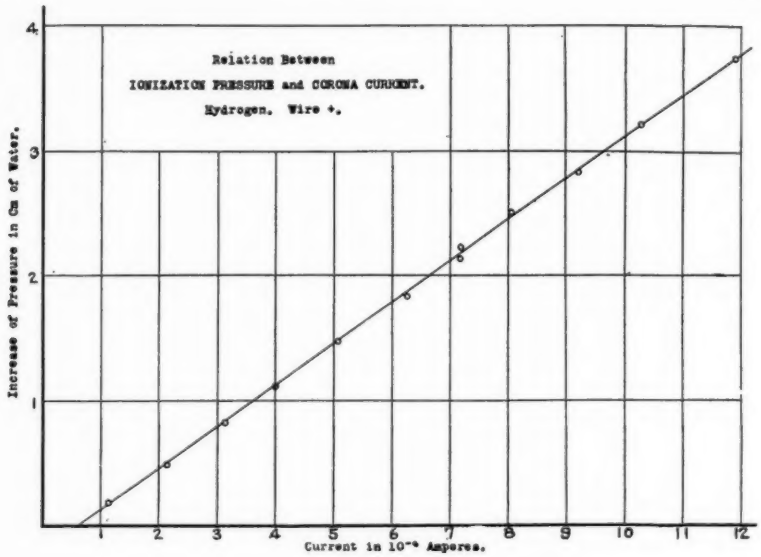
Relation Between
IONIZATION PRESSURE and CORONA CURRENT.
Hydrogen. Wire +.
Increase of Pressure in Cm of Water.
Current in 10⁻⁶ Amperes.

Fig. 5.

wire positive *the ionization pressure is exactly proportional to the corona current.*

In the case of oxygen a considerable amount of ozone was formed due to the corona discharge. Evidently the curve as shown is a resultant of two effects: (1) A chemical change due to the formation of ozone. This would tend to cause a decrease in pressure. (2) The increase in

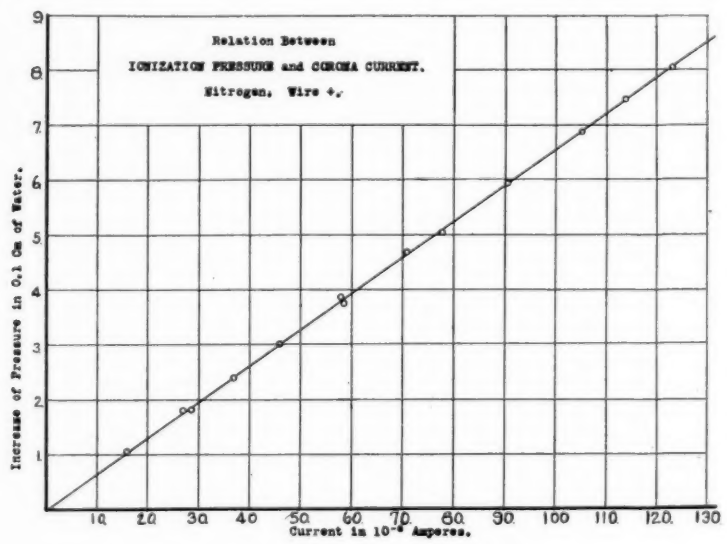
Relation Between
IONIZATION PRESSURE and CORONA CURRENT.
Nitrogen. Wire +.
Increase of Pressure in 0.1 Cm of Water.
Current in 10⁻⁶ Amperes.

Fig. 6.

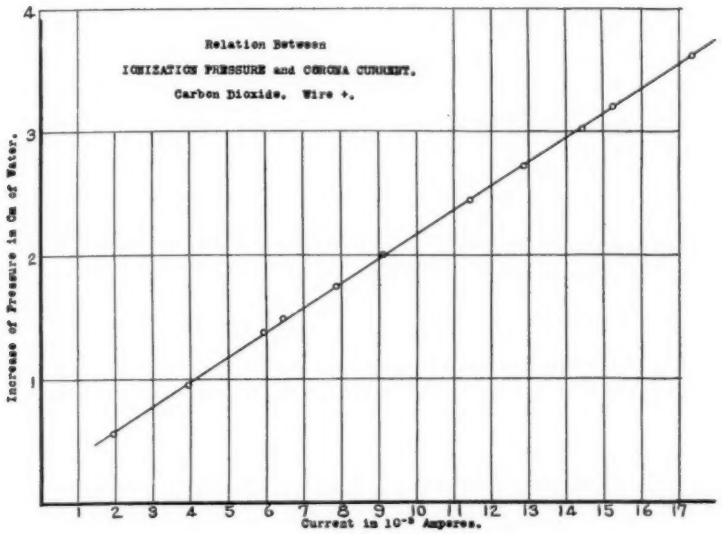
Relation Between
IONIZATION PRESSURE and CORONA CURRENT.
Carbon Dioxide. Wire +.
Increase of Pressure in Cm of Water.
Current in 10⁻⁵ Amperes.

Fig. 7.

pressure due to the ionization of the oxygen. Since the ionization curve is a straight line, as is shown by the gases in which probably there is no chemical action, and since this resultant curve of oxygen is a straight line, the following law can be stated:

Whenever chemical change takes place due to the corona the chemical change is exactly proportional to the current.

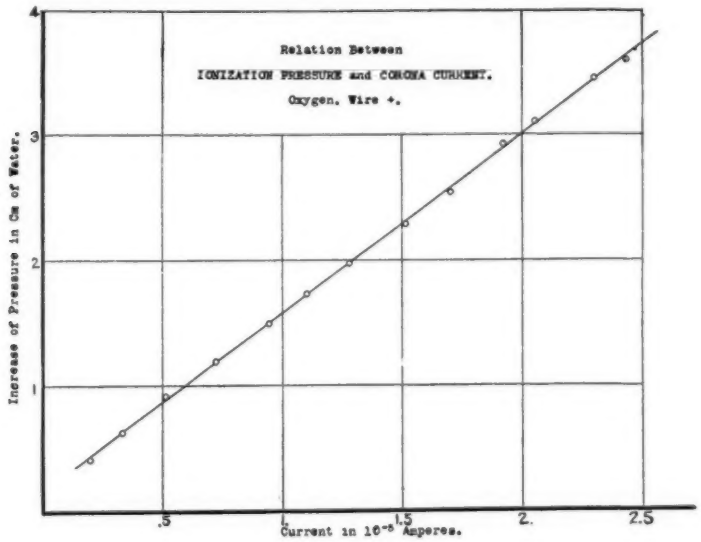
Relation Between
IONIZATION PRESSURE and CORONA CURRENT.
Oxygen. Wire +.
Increase of Pressure in Cm of Water.
Current in 10⁻⁵ Amperes.

Fig. 8.

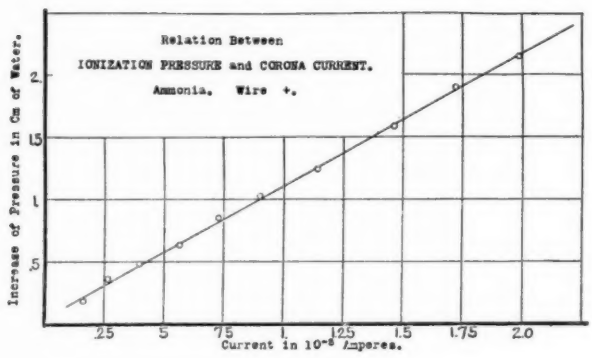

Fig. 9.

With the wire negative beads always appear on the wire, and since the pressure increase varies with the arrangement of the beads which are not stable, it is impossible to accurately verify the above relationship. When, instead of the quick acting gauge, an ordinary open manometer which is slow in its action was used, it was discovered that the same relationship as above stated is very nearly true for the wire negative as well as positive.

The increase in pressure in the case of nitrogen, showing ionization, is one of the exceptional cases where nitrogen is largely ionized at low temperatures and thus probably chemically active.

How nitrogen, carbon dioxide and ammonia are ionized, are questions which require further study.

The arrangement of the apparatus could be used as a high potential voltmeter by simply calibrating the increase in pressure against volts, as determined by a disc electrometer.

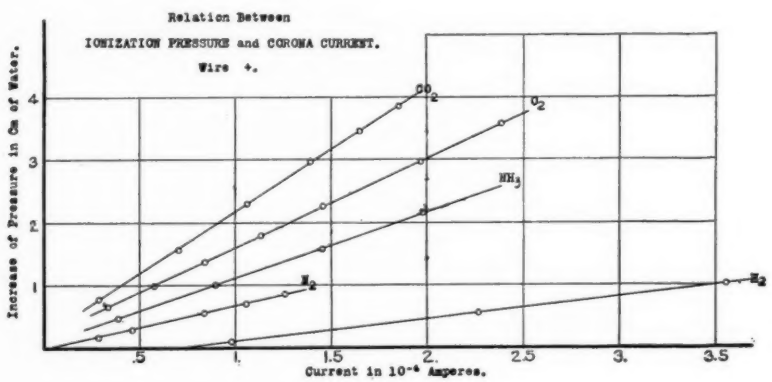

Fig. 10.

SUMMARY.

The ionization pressure in the positive corona is exactly proportional to the corona current in dry air, hydrogen, nitrogen, carbon dioxide, oxygen and ammonia.

Any chemical action that takes place due to the corona is exactly proportional to the corona current.

The writer wishes to acknowledge his indebtedness to Professor A. P. Carman and to Dr. Jakob Kunz, associate professor of physics, for their deep interest and helpful suggestions concerning the conduct of this work.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
May, 1916.

ON THE INFLUENCES CONTRIBUTING TO THE VARIATION OF CONTACT ELECTROMOTIVE FORCE WITH TIME.[1]

BY OTTO STUHLMANN, JR.

IF a freshly cut zinc surface is placed in a vacuum opposite a copper plate and light of frequency ν is allowed to fall on the zinc surface, the electrons thus emitted will leave the plate with energy

$$\tfrac{1}{2}mv^2 = h\nu - \omega,$$

where h is the Planck constant and ω a constant peculiar to the metal. Richardson[2] has identified ω with the work done by an electron, starting from the interior, in crossing the surface of the conductor. Using a statistical method and thermodynamical arguments he obtains the relation

$$V - V' = \frac{1}{e}\left\{ \omega - \omega' + R\theta \log \frac{n'}{n} \right\},$$

where $(v - v')$ represents the contact difference of potential between the two metals in terms of the difference between the work done by an electron in crossing the boundaries of the respective metals, plus an expression representing the Peltier effect. This last term is small compared to the contact difference of potential and will be neglected. This interpretation has found support through the experiments of Richardson,[3] Compton, Cooke, Wilson and others.

A second interpretation of the constant ω has recently been adopted by Millikan.[4] His view point is taken from the interior of the metal. He assumes ω to represent the sum of two independent quantities p_1 and p_2. Where p_1 represents the work necessary to just separate the electron from the atom, and p_2 the work necessary to separate it from the metal so that an accelerating field can remove it.

Using this conception we may define the contact difference of potential as

$$V - V' = \frac{p_2 - p_2'}{e}.$$

[1] An abstract of this paper was presented before the Am. Phys. Soc., April 21, 1916.

[2] Richardson, Electron Theory of Matter, p. 455.

[3] See Richardson's Electron Theory of Matter.

[4] Millikan, PHYS. REV., 7, p. 27, 1916.

If we now let ν_0 and ν_0' represent the frequencies of the long wave-length limits at which the photoelectric action of the two metals under comparison just ceases, we may write for the values of ω and ω' in Richardson's equation the values

$$\omega = h\nu_0 = p_1 + p_2,$$
$$\omega' = h\nu_0' = p_1' + p_2',$$

which in connection with the above definition gives us Millikan's equation for the C.D.P. in terms of Einstein's equation,

$$V - V' = \frac{1}{e}(h\nu_0 - p_1) - (h\nu_0' - p_1').$$

A conception of the contact difference of potential between two metals, in terms of the difference between the amount of energy removed from the incident beam of light and the energy of separation of the electron from the atom. Millikan's results show a very close agreement with his theory, in some cases the difference between the C.D.P. measured directly and that computed from a simplified form of the above equation check within one per cent. This evidence more than any other gives us a direct proof of an intrinsic contact difference of potential other than that induced by exterior or interior chemical effects.[1]

A somewhat similar argument, though not involving the definition of C.D.P. as given by Millikan, was published by Einstein.[2] He assumed the existence of a "double layer" at the metal-dielectric boundary, which gave rise to the C.D.P. It was situated so that its negative surface was always away from the metal. Experimental evidence for the existence of such a double layer may be found in the recent literature dealing with the photoelectric effect.[3] An electron, Einstein concludes, in leaving the metal can only do this if it overcomes the potential gradient V existing in the double layer. The energy eV to do this is only attained when the frequency of the incident light has a value given by

$$eV = h\nu.$$

In a similar way a second metal possessing a double layer of gradient V' can only lose an electron through a frequency ν'. Hence

$$V' - V = \frac{h}{e}(\nu' - \nu)$$

represents the equivalence of this contact difference of potential. This

[1] For a summary of the arguments "Chemical C.D.P. versus Physical C.D.P." see Oliver Lodge, Phil. Mag., XLIX (1900).

[2] Ann. d. Phys., 20, p. 203 (1906).

[3] Stuhlmann and Compton, PHYS. REV., 2, p. 199 (1913). Seeliger, Phys. Zeit., XIV., p. 1273 (1913). Compton and Ross. PHYS. REV., 6, p. 207 (1915).

relation, like that of Millikan's, shows that the red wave-length limit of the incident light producing photoelectrons, moves towards the region of smaller frequencies as the contact difference of potential between the two metals increases towards positive values. This important point will be reconsidered when we investigate the data showing the effect of the accumulation of gaseous layers of variable concentration on the surfaces of metals and their influence on the C.D.P.

A final, though none the less important, point of view must be considered, namely that obtained when investigating the C.D.P. from without the metal. This group of literature, since Lodge's classical summary, is unique in its seeming contradictions. In a general way the data dealing with the causes of the variation of C.D.P. may however be divided into two groups.

First that group of investigations which show that the C.D.P. will gradually increase with time. The equilibrium value resulting in a greater electronegative or electropositive value, depending on the method used in cleaning the surfaces under investigation. Their gradual change to a steady value has been definitely observed by Shaw.[1] He attributes this change to the presence of charged surface layers. The rate of charging or removal of layers responsible for the C.D.P. is shown to be independent of the metal and identical with the behavior of ordinary charges imparted by external means. More recently Compton[2] had determined an empirical relation between C.D.P. and time in the form of an exponential equation. To attribute such a change to a local chemical action seems improbable from the data submitted.

Second that group which has observed fluctuations of the contact electromotive force in the presence of gases to such an extent that no positive conclusions can be drawn concerning the seat of the electromotive force. Such seemingly inconsistent results were usually attributed to " insoaked air films " on the surface of the metal. Spiers[3] also has shown that films of hydrogen on the surfaces of the metals tend to move their C.D.P. to more electronegative values, while air films tend to make them more positive. That temporary high potentials are attained when a metal is burnished, that no two methods of cleaning a surface produces the same value of the C.D.P. and that all experiments show fluctuations of the potential with time, with no tendency for the voltage to settle to a final steady value.

The most important advance seems however to have been made by

[1] Shaw, Phil. Mag., 25, p. 241 (1913).

[2] Compton, PHYS. REV., VII, p. 212 (1916).

[3] Spiers, Phil. Mag., 49, p. 83 (1900). See also Broglie, C. R., 152, p. 696 (1911).

Beil,[1] at the instigation of Hallwachs, who had observed the fluctuations of the contact electromotive force in connection with his photoelectrical work. Beil observed a fatigue of the contact electromotive force of zinc in the presence of water-vapor. He attributed it to the formation of hydrogen on the surface of the metal. This explanation seems to be supported by the experiments of Russel.[2] The observed decrease in the case of zinc was of the order of magnitude of about .2 volt during the first half hour. In the interior of a closed vessel this decrease was lessened. He also showed that the smaller the vessel the more electronegative the change and that eventually the change was in an electropositive direction for very small vessels. This in conjunction with his experiments on the effect of dry and moist air led him to the conclusion that dry air acts like a small vessel changing the C.D.P. to more electropositive values while moist air acts like a large vessel, producing more electronegative values with time. The action was traced to the influence of water-vapor, or carbon dioxide in the presence of water-vapor and the lessening due to the smaller motion of the air.

The photoelectric aspect, seemingly promising, throws very little if any light on the influences at work which change the contact electromotive force with time. It therefore becomes of interest to attack the causes of the change from a point of view exterior to the metal, with the hope that the seeming contradictory results possess some common underlying generalization.

The measurements to be described in the following pages were made in a copper cylinder, Fig. 1, oxidized to a matte black. No solder was exposed on the inner side and all grease was carefully removed. This produced a stable and dense surface practically incapable of occluding gases. In a previous experiment where it had served as part of a photoelectric cell it had been noted for its constancy of contact electromotive force in photoelectric velocity measurements. The metal under examination was placed coaxial to the cylinder. It was either in the form of a rod, or a thin narrow strip of the material. This was attached to a screw clamp of brass which was insulated from the cylinder by means of a high-grade, hard red sealing wax. The rod led to the electrometer calibrated to read volts (776 div. per volt). All parts of the apparatus except those between which contact electromotive force is measured must be covered with hard sealing wax so as not to influence the results. The only opening in the cylinder was a one-centimeter hole, leading to a molecular pump used to remove the gases as occasion demanded.

[1] Beil, Ann. d. Phys., 31, p. 489 (1910).

[2] Russel, Proc. Roy. Soc., 63, p. 109 (1898).

Two methods of measurement were reported to and were used as checks where experimental conditions warranted.

The usual method consisted in noting every thirty seconds the increments in potential of the electrometer. Under these operating conditions[2] the cylinder was maintained at zero potential and the ionization current was supplied by a constant source of gamma rays placed at *S*. As a check to these readings a compensation or null method was used. For this purpose the cylinder was connected to a potentiometer circuit, and the potential adjusted so that no current passed between the cylinder and plate. The applied potential as indicated on a standard Weston voltmeter gave the magnitude of the contact difference of potential under observation. These measurements were made to two one thousandths of a volt.

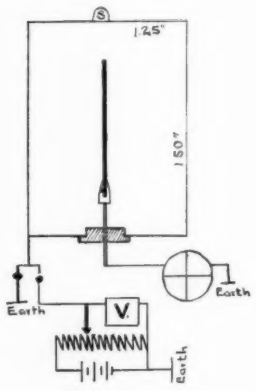

Fig. 1.

Sources of Error.—Owing to the appreciable capacity of the system and intentionally chosen small ionization current, the rate of charging the electrometer is in many instances rather slow. Its readings starting from zero increase exponentially with time, although the contact difference of potential does not possess a zero value, for time equal to zero. The readings therefore will only indicate changes in this exponential charging of the electrometer. It was early discovered that no other sources of contact electromotive force must exist in the circuit containing the metal under observation. Such stray electromotive forces may account for the many and curious variations superimposed upon the normal course of events occurring in the test chamber. It is important that the radium source is so protected that no ionization can take place outside of the restricted volume of the cylinder. The source *S* must also be placed centrally and symmetrically to the metal under examination, so that the ionization may be uniform throughout the volume of the gas.

General Results.—The metals platinum, carbon, palladium, copper and zinc were examined. The first three of this group were chosen for their pronounced property of occluding gases, the last two because of the known investigations of other observers. All data on these metals, arbitrarily as to the history or method of treatment before contact measurements were made, were found capable of classification into two

[1] N. Shaw, loc. cit.

[2] Kelvin's ionization method, Phil. Mag., 56, p. 82 (1898).

groups. The first group was of the type illustrated by the simple exponential curve in Fig. 2. If no impurity were added to the surface in the form of alcohol, water or oil, all metals investigated in the presence of pure dry air, arbitrarily as to how they were cleaned, produced the simple exponential rise of the electrometer with time. The second group of results possessed characteristic variations due to the presence of water-vapor in the gas surrounding the metal. These variations were often very complex. An initial rise in potential was followed by a corresponding fall or vice versa. Often this double change would lead to a complete reversal in sign of the contact difference of potential. It was found that the results leading to the more complex variations were always due to

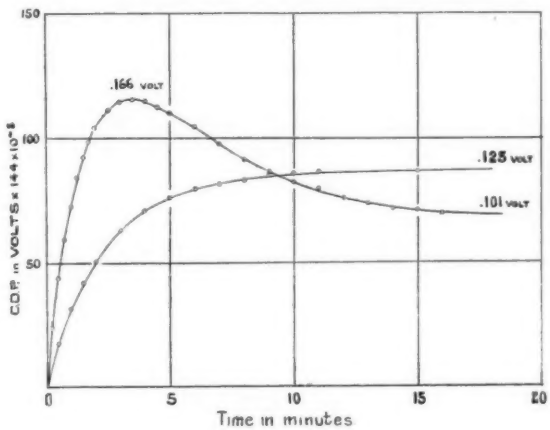

Fig. 2.

some exterior, controlable cause other than that taking place at the surface of the metal. In the final analysis these curves were all reducible to the simple double exponential type shown in Fig. 2.

Variations in the surface conditions, however, change the value of the constants of the pure exponential curve, so that no two treatments of the same metal produce the same equilibrium values. In the presence of water-vapor this was found to be even more pronounced. For instance the difference between the equilibrium values for a burnished and scraped platinum plate examined in the presence of water vapor, not only produced an increase of several tenths of a volt in the end value but also a decrease of two tenths of a volt in the maximum.

Results from Carbon and Dry Hydrogen.—In view of the recent data from the photoelectric effect it is allowable to assert that the contact difference of potential has its origin in the immediate surface and not in the interior of the metal. If therefore a metal is chosen, whose surface

characteristics can be controlled without producing changes such as accompany scraping or polishing, the above results could possibly be more easily analyzed. Now charcoal possesses to a marked degree the property of occluding gases, resulting in changes in the concentration of the gas, forming the surface layer of the material.

In this connection Berger[1] has shown that cocoanut charcoal will absorb as much as 24 c.c. of air per gram of charcoal at 18° C. and 752.9 mm. of pressure. If the carbon is heated to 550° C. and cooled in vacuo, its ability to absorb air increases exponentially with time, which reaches its maximum in about sixty minutes. For different gases the amount absorbed depends largely on the pressure of the gas.

To produce the necessary cocoanut charcoal, of a uniform texture and known previous history; a large and very thick cocoanut shell was broken into large pieces and carbonized in an electric furnace, then cooled with the exclusion of air. The largest pieces were now cut and sandpapered into thin strips, one half centimeter wide, about three centimeters long and one millimeter thick. These strips were placed in the clamp as shown

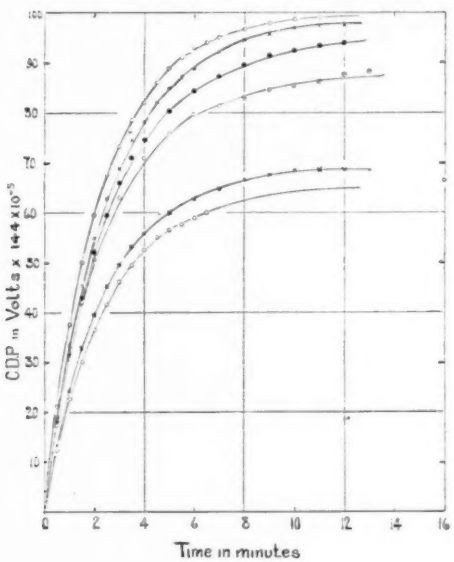

Fig. 3.

in Fig. 1, and connected to the electrometer. The apparatus was evacuated by means of a molecular pump until the pressure was reduced to 10^{-6} cm. or less. Initially the carbon gave off a considerable quantity of gas which upon spectroscopic examination showed complex hydrocarbon bands; this evolution of gas gradually decreases and eventually

[1] F. Berger, Ann. d. Phys., 37, p. 472 (1912).

disappears. Pure dry air is now introduced into the cylinder and allowed to stand for half an hour. This cleaning of the carbon plate was repeated until the gas pumped off was spectroscopically free from gases other than air. The drying took place through a liter Wolf bottle filled with concentrated sulphuric acid, from which the air passed through a thirty-centimeter tube of lump calcium chloride, thence through a three-meter tube of phosphorous pentoxide two centimeters in diameter.

The carbon was now examined for contact electromotive force in this dry air. The resulting charging of the electrometer with the equilibrium value attained is shown in the upper curve of Fig. 3.

If a small amount of dry pure hydrogen, made from chemically pure zinc and sulphuric acid, is now introduced into the cylinder, the hydrogen will be occluded at the expense of the air. The mixture was allowed to stand over night, after which it was assumed equilibrium had been established. The contact electromotive force was then determined. Under these conditions the second curve from the top was generated, the equilibrium value becoming more electropositive by 178×10^{-5} volts. Successive increases in concentration of the hydrogen produced the successive lowering of the equilibrium values, until a point was reached where the absorbed gas was only pure hydrogen, when no further lowering of the end value occurred. The final value was .0489 volt lower (more electropositive) than the initial contact difference of potential when no hydrogen was present. To check these results, the experiment was now reversed. The hydrogen was gradually pumped off and replaced by air. This decrease in concentration of the hydrogen resulted in a similar series of curves ending in the initial results of the previous experiment. This final value was not attained, however, until the carbon had been baked in an electric vacuum furnace.

The other metals were cleaned with glass paper, another series scraped with a steel tool, and then examined under similar conditions explained above. They exhibited changes similar to those shown by the carbon but neither were they so pronounced nor was the occlusion of hydrogen so simply controlled.

The experiment was also repeated with cocoanut charcoal, whose gas had been removed through heating (above 550° C.) in an electric vacuum furnace. These results contributed nothing to those quoted above.

Results from Carbon Saturated with Other Gases.—Similar pieces of charcoal from the same stock were now examined for changes in contact difference of potential in the presence of and saturated with dry ozone, oxygen, air, carbon dioxide, nitrogen and ammonia. The curves resulting through the presence of these gases in the carbon are shown in Fig. 4.

The carbon was not only saturated with the gas, but the measurements were also made with that particular gas filling the chamber. Any other combination, such as replacing the gas in the chamber by means of dry

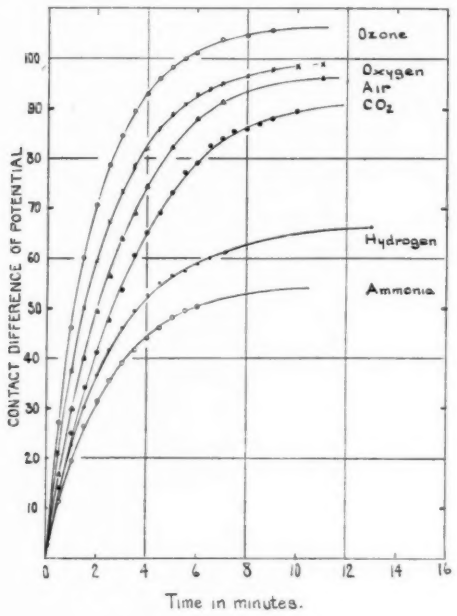

Fig. 4.

air, resulted in diffusion of the occluded gas from the carbon, accompanied by a corresponding upward shift of the values, as shown with hydrogen. The curve for nitrogen was omitted due to its proximity to that of carbon dioxide.

The ozone used in these experiments was collected from the immediate vicinity of a 110-volt quartz mercury vapor lamp. The lamp was inclosed in a small box and the gas drawn out of this compartment, after the lamp had been burning several hours. This and the other gases were all dried through the phosphorous pentoxide tube described. The oxygen was the commercial type derived from liquid air. The nitrogen was generated by heating ammonium nitrite. It was purified by passing it through sodium hydroxide and thence over glowing copper gauze. The ammonia was acquired by heating chemically pure concentrated ammonium hydroxide and then dried in the usual way.

The order in which the equilibrium values of the carbon, saturated with these gases appear, is of interest in so far as they are identical with the Volta series for these gases as determined by Grove,[1] in his experiments

[1] Grove (Phil. Trans., 1845), Winkelman's Handbuch, Vol. 2, Elect. and Mag., p. 181.

on gas cells. Similar series by Becke[1] and Gore[2] are quoted for comparison. The last column in the table shows the observed equilibrium value of the contact electromotive force in volts, attained by the carbon, satu-

Volta Series for Gases.

Grove.	Becke.	Gore.	*S*	Equilibrium Values in Volts.
+				
Metals that decompose water				
NH_3			NH_3	.079
H_2	H_2	H_2	H_2	.096
CO				
Alcohol				
Aether				
Camphor				
Metals insoluble in water				
N_2		N_2	N_2	.129
CO_2	Air		CO_2	.130
NO	CO_2		Air	.136
O_2			O_2	.142
O_3			O_3	.155
I		I		
Br		Br		
Cl		Cl		
		O_2		
—		Fl		

rated with these gases, when the opposing plate of copper oxide was at a zero potential.

It might be of interest to compare the value obtained for " air " with that computed from the values of nitrogen oxygen and carbon dioxide, taken in the proportion in which they occur in air.[3] The latter gives .132 volt as against the observed value of .136 volt.

Conclusions in Regard to the Effect of Dry Gases.—In view of the above data it seems essential to know or be able to control the previous history of a metal before values of contact electromotive force can be accepted with any reliability. The intrinsic potential can be determined only after all occluded and surface gases are removed. That the removal of all gases is difficult and often impossible, was shown by the recent experiments of Hughes.[4] He has shown what a tremendous influence the entrance of the slightest trace of air may have on the contact potential

[1] A. Becke, Ann d. Phys., 29, 5, pp. 909–940 (1909).

[2] G. Gore, Cooper's "Primary Batteries," p. 19 (1901).

[3] Phys. Chem. Const., Kaye and Laby, p. 125. Composition of air by volume, N_2 78.05, O_2 20.91, CO_2 .03 to .3, A .95.

[4] Ll. Hughes, Phil. Mag. (6), 28, p. 337 (1914).

of metals distilled in a very high vacuum. Another point of interest, in this connection, is the supposed absence of gases on the surfaces of metals like Na, K and Li freshly cut in vacuo.[1] The surfaces are not here necessarily exposed to the residual gases in the vessel, they are however exposed to the occluded gases which constantly leak to the surface from the depths of the metal itself.

In a very exhaustive paper Murray[2] showed that if a plate of zinc is polished with glass paper, it attains a potential .70 volt positive to a standard gold plate. If it is now burnished with a tool of hardened steel it will rise to a nearly permanent value of .94 volt. This "seeming inexplicable[3] electropositive increase" of .24 volt through burnishing can however be explained in terms of our occlusion experiments. They show that, as the concentration of the hydrogen occluded near the surface increases, the equilibrium values become more electropositive. Now zinc in common with all other metals can occlude gas to a certain extent. The surface layer of the zinc, under the influence of the pressure exerted by the burnishing tool becomes more compact. This packing is accompanied by a corresponding concentration of the occluded gas in this layer. Hence such and other mechanical concentrations must necessarily result in a more electropositive value for the contact potential.

In a similar way all mechanical processes that produce fresh surfaces on a metal, through the removal of the old one, must result in a gradual accumulation of gas on this new surface, which again results in a positive shift of the C.D.P. And a shift to more positive values in the C.D.P. gives us a corresponding shift of the red wave-length limit towards positive values as Millikan[4] has recently shown, in his experiments on the photoelectric effect. A similar photoelectric shift should result if a metal originally having occluded a very electronegative gas, had that gas replaced by means of a very electropositive one.

The above parallelism between photoelectric shift in the red wave-length limit and contact difference of potential is very interesting, since it leads us to think that the occlusion of gases, up to a certain degree, offers the electrons in the metal a means of decreasing their affinity for the atoms.

Experiments on the Influences of Water-vapor.—If water-vapor had been present in the gases during the previous experiments, the variations of the contact electromotive force would have been more complex. The

[1] K. T. Compton, Phil. Mag. Ap., p. 579 (1912). R. A. Millikan, PHYS. REV., 7, p. 366, also p. 374 (1916).

[2] E. Murray, Proc. Roy. Soc., 63, p. 113 (1898).

[3] Lodge, Phil. Mag., XLIX., p. 371 (1900).

[4] R. A. Millikan, loc. cit.

results obtained under these conditions have, however, some things in common. Independent of the kind of metal or gas used, what at first sight passed for contact electromotive force, rises to a maximum and then gradually drops off to an equilibrium value, as time goes on.

Similar variations have been observed by investigators referred to above. More recently Lose[1] has found similar variations in his experiments on the influence of glow-discharge on the volta-effect.

After eliminating all extraneous causes of contact electromotive force and using very pure gases in the presence of water vapor, one finds that the complex variations can in general be represented by such a double exponential curve as shown in Fig. 2. The curve with increasing values of time was found to rise exponentially to a maximum, then fall off exponentially to an equilibrium value. The initial rise is similar to that discussed under the effect of dry gases, superimposed on this effect is the exponential decrease due to the presence of the vapor.

In the presence of any of the above gases and water-vapor similar variations are observable, but the magnitude and appearance of the maxima, and the absolute value of the end or equilibrium values are different.

Cocoanut charcoal was again resorted to in studying this effect. The strip of gas-free carbon was placed in the chamber and the gas under examination mixed with water vapor was allowed to enter the vessel. Later this was varied by examining the carbon in the presence of the dry gas, then reëxamining it when a few drops of water were introduced into the bottom of the cylinder. This was enough to produce the desired saturation at room temperature. For the sake of clearness only a few of the representative values are given. The first curve to the left in Fig. 5 showing a pronounced maximum was obtained in the presence of air and saturated water vapor. The curve rises to a maximum of $-.141$ volt after 52 seconds from the time at which the carbon's potential became active through opening of the earthed key connecting the plate to the electrometer, from this point the potential gradually fell to -0.014 volt after an elapse of six minutes. The curve below it shows the results obtained when the air is replaced by hydrogen also saturated with water-vapor. The maximum is not so pronounced and only attained -0.0391 volt after 200 seconds. Similar experiments with platinum and palladium produced similar effects though the maxima and end values were different.

Experiments with Other Vapors.—The second series shown to the right in Fig. 4 represents identical experimental conditions as the previous ones,

[1] A. S. Lose, Deutsch. Phys. Ges. Verh., 17, 1, p. 3 (1915).

with this exception, alcohol-vapor was substituted for water-vapor. All the maxima were higher and the time of their appearance was very much greater. The end values, even after several hours, were not as low as those reached by the metal in the same gas saturated with water-vapor. Experiments with the vapors from turpentine and soft wax produced still larger changes in the time of appearance of the maxima. In addition the rate of increase and decrease of the potential near the maxima is very slow and often imperceptible; so much so that the results may be mis-

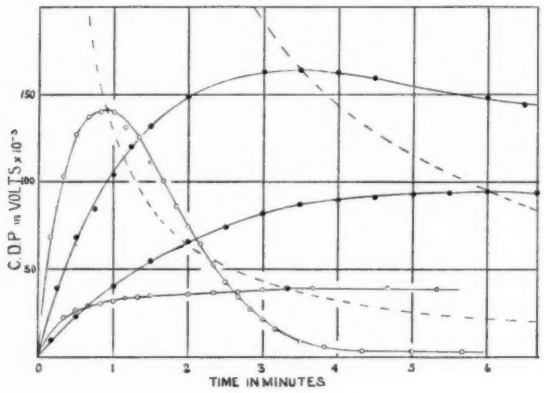

Fig. 5.

taken for the pure exponential curves common to the results discussed under variations in the presence of dry gases.

The above series and similar ones for other metals, lead to some very interesting conclusions in regard to what have heretofore passed as contact electromotive forces. The subsequent lowering of the contact potential has usually been attributed to the presence of hydrogen peroxide. The hydrogen peroxide was assumed to attack the metal and form a secondary reaction, resulting in the change leading to an equilibrium value. This secondary reaction is however improbable in ammonia or nitrogen saturated with water-vapor or alcohol-vapor, in which nevertheless the rise to a maximum and subsequent drop to an equilibrium value occurs. Of course one might argue for the presence of this secondary reaction through the well-known catalytic power of carbon or platinum. But would such a reaction result in the formation of a free charge, contributing its share to the charge accumulated by the electrometer?

A more promising explanation is offered when we consider the possibilities introduced by the polarization of the metal surface under investigation.

Polarization Theory.—In a primary cell, the reduction in the electro-

motive force due to an alteration of the electrolyte or of the plates, brought about by the voltaic action of the cell is known as polarization.[1] Our experimental conditions are such that they may be considered acting like a primary cell, the necessary current being supplied by the constant source of ionization. This ionization current may be considered as moving towards the carbon plate under the action of the potential gradient due to the intrinsic contact difference of potential between it and the copper oxide cylinder. The cylinder is constantly kept at a zero potential, while the carbon plate, initially at zero, is connected to the electrometer when the circuit is under examination. The electrometer therefore measures the variations taking place at the carbon plate and at such points in its immediate neighborhood as can influence its potential.

Let us first consider the conditions involving no polarization, namely, those results obtained from the variation of the contact difference of potential in dry gases. The exponential curve attains a maximum potential V' after an infinite time. Let V be the instantaneous value of the potential as indicated by the electrometer. Let the system have a capacity C such that $Q = Ne = CV$. Then

$$\frac{dN}{dt} = \frac{C}{e}\frac{dV}{dt}.$$

Let

$$\frac{dN}{dt} \propto (V' - V);$$

then

$$\frac{dN}{dt} = k(V' - V) \qquad (1),$$

where the constant k denotes the rate of appearance of the ions at the plate, it also depends on c/e, on the kind, concentration and density of the gas, on the velocity of the ions, etc. Solving[2] this equation for the instantaneous value that the potential may attain, we get

$$V = V'(1 - e^{-kt}), \qquad (2),$$

an expression which when plotted corresponds to our various curves for dry gases. For example the hydrogen change in concentration curves may now be represented by simply varying the values of k in the above equation. Increasing values of this constant takes us step by step from the lowest curve, representing maximum concentration, to the highest one, representing zero concentration. Hence k is inversely proportional to the property of the occluded gas, contributing to the variation from the intrinsic contact potential.

[1] Cooper, Primary Batteries, 1901.

[2] I am indebted to Professor Horace C. Richards for valuable suggestions involved in this analysis.

If a vapor is now introduced, our experimental values lead to a secondary reaction resulting in polarization. Under these conditions the above V' becomes a variable, through the variation contributed by the polarization. Again let

$$\frac{dV'}{dt} = -k'V',$$

where the negative value of the constant k' denotes the rate of decrease through polarization action. It also depends on the current density, temperature, character of the electrode, etc. Solving for V' we get

$$V' = V_0 e^{-k't}, \tag{3}$$

which in combination with equation (1) gives

$$\frac{dV}{dt} + kV = kV_0 e^{-k't}, \tag{4}$$

whose solution is

$$V = V_0 \frac{k}{k + k'} (e^{-k't} - e^{-kt}) \tag{5}$$

where the constant V_0 is the contact difference of potential when the polarizing influence is removed. This is the double exponential curve which fits all the results when polarization takes place through the presence of a vapor.

The equation has a maximum for values of t given by

$$\frac{k'}{k} = e^{(k-k')t}.$$

This result posesses a special interest in so far as it states that the maxima of all curves developed from any particular metal in the presence of any gas, saturated with a particular vapor, must lie on the logarithmic curve characteristic of this group of limitations. For example if $k'/k = 68.5$ and plotting k' against time we get the dotted logarithmic curve passing through all the maxima of the left group. For the above ratio equal to 6,380 we get a corresponding curve through the maxima of the group on the right.

Intermediate values of this ratio produce corresponding curves passing through the maxima of the curves from the various mixtures of concentrations of alcohol and water.

Conclusions.—Variations in contact difference of potential of a specific metal are primarily due to the kind and concentration of the occluded gas in the metal.

Successive increases in concentration of the occluded gas produce successive decreases in the electronegative magnitude of the contact difference of potential, a property common to all gases.

All mechanical processes affecting the surface layers of the metal tending to increase the concentration of the occluded gas produce the same change.

The gases ozone, oxygen, air, carbon dioxide, nitrogen, hydrogen and ammonia if occluded by a metal, shift the position of the metal in the Volta series to a more electropositive value in the order in which they are named. Changes in contact difference of potential were found for gases and vapors which cannot form hydrogen peroxide to explain the secondary reaction. These and similar changes in contact difference of potential involving secondary reactions, can be explained with a polarization hypothesis.

The degree of polarization depends on the relative electronegative properties of the gases and vapors in which the contact difference of potential is measured.

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THE NORMAL PHOTOELECTRIC EFFECT OF LITHIUM, SODIUM AND POTASSIUM AS A FUNCTION OF WAVE-LENGTH AND INCIDENT ENERGY.

BY WILMER H. SOUDER.

INTRODUCTION.

THE original photoelectric discovery by Hertz[1] in 1887, which was extended by Hallwachs[2] in 1888, indicated a property possessed by metals whereby they may emit negative electricity when illuminated by light. Experimental work looking toward a satisfactory explanation of this phenomenon has not yet furnished the complete solution. With continued study this apparently simple effect has continued to branch until it now includes many factors which at first were considered unimportant. Consequently apparently similar researches have often yielded quite contradictory results. The experiments of Pohl and Pringsheim[3] showing two distinct modifications of the photoelectric effect, viz., the normal and selective effects, have been efficient in harmonizing many of these supposed contradictions.

However the results submitted in this paper raise a question as to whether or not their definitions of the normal and selective effects are complete.

THE NORMAL AND SELECTIVE EFFECTS.

The criteria which they give for these effects in terms of energy content, wave-length, angle of incidence and plane of polarization are:[4]

"The normal effect extends from an upper limit (of wave-length) determined by the electro-positive character of the metal, downward over the entire short wave-length spectrum. The number of electrons emitted per unit of absorbed energy increases constantly with diminishing wave-length, and the orientation of the light vector influences the number of electrons only in so far as it conditions the absorption of the light.

"The selective effect on the other hand is confined to a narrow wave-length interval. Here the effect experiences an increase indicating re-

[1] H. Hertz, Ann. d. Physik, 31, 421 and 983 (1887).

[2] W. Hallwachs, Ibid., 33, 301 (1888).

[3] R. Pohl and P. Pringsheim, Die lichtelektrischen Erscheinungen.

[4] Ibid., Ber. D. physik Ges., 12, 682 (1910).

sonance, but only when the orientation of the light vector allows a component of the electric field strength perpendicular to the metal surface." They locate this selective maximum for four alkali metals at the wave-lengths indicated in Table I.

TABLE I.

Metal.	Wave-length.
Rubidium	475$\mu\mu$
Potassium	440
Sodium	340
Lithium	280

On surfaces of aluminum and magnesium[1] they found maxima appearing after about twenty-four hours at about 250 $\mu\mu$ and 240 $\mu\mu$ respectively. These maxima were not considered as locating a selective effect, for changing the plane of polarization did not affect the curve. A calcium[2] surface showed a similar effect at 360 $\mu\mu$. Additional tests showed the maxima more pronounced for light normal to the surface. They explain this as due to the greater penetration of short wave-lengths which liberate electrons at so great a depth that many of them do not reach the surface.

Compton and Richardson[3] obtained surfaces of aluminium, sodium and potassium by distillation upon a curved strip. Then using isotropic radiation found, when they plotted photo-current per unit of incident energy against wave-length, that there was a maximum for aluminium at 220 $\mu\mu$. For sodium they found maxima at two points, viz., 225 $\mu\mu$ and 360 $\mu\mu$. They also found a maximum at 250 $\mu\mu$ for cæsium.

The purpose of the following experiment was to investigate the photo-current per unit of incident energy as a function of wave-length using normal incidence on new surfaces of potassium, sodium and lithium formed by shaving in vacuo.

APPARATUS AND EXPERIMENTAL ARRANGEMENT.

The photo-cell was the same as that recently described by Professor Millikan.[4] New surfaces of the metals were obtained by cutting in vacuo. A 12 centimeter mercury arc in quartz (Heræus type) served as the source of illumination. The light resolved by a Hilger monochromatic illuminator was unpolarized except for such polarization as is due to transmission and reflection at the surface of the prism or mirror. Below 365 $\mu\mu$ the slit was $\frac{1}{2}$ mm., elsewhere $\frac{1}{4}$ mm. Photocurrents were measured by a Dolezalek quadrant electrometer, charged to give 850 mm. deflection at a distance of one meter when a potential difference of one volt was

[1] Ibid., 14, 546 (1912).

[2] Ibid., 15, 111 (1913).

[3] K. T. Compton and O. W. Richardson, Phil. Mag., 26, 549 (1913).

[4] R. A. Millikan, PHYS. REV., 2d Ser., 7, 355 (1916).

applied to the terminals. A ten-element thermopile having a resistance of 2.8 ohms was used for energy measurements. The galvanometer[1] used with this thermopile had a resistance of 2.5 ohms for coils in parallel and was made specially for this experiment by Dr. Colentz with the view of obtaining the highest sensibility possible. The suspension consisted of eight magnets and a mirror mounted on a quartz rod which in turn was suspended by a quartz fiber. The total weight of this suspension was less than five milligrams. A sensibility of 1×10^{-11} was obtained; though this was higher than it was found necessary to use in most of the measurements, since the purity of the wave-length at weak energy positions may be questioned (see below). Since the scale was two meters distant it was to be expected that galvanometer deflections, up to at least 50 cm., would be proportional to incident energy, but this was established by direct experiment in two ways. First, the galvanometer deflections were found by a potentiometer to be proportional to E.M.F., and E.M.F. temperature relations are always linear for small temperature intervals. Second, photo-currents are known to be proportional to incident energy. When the incident energy of the green mercury line was changed by inserting absorbing surfaces, the ratio of photo-current to galvanometer deflection was found to be constant. The electrometer deflections were shown proportional to photo-current by varying the time of illumination, using a selected wave-length. In all cases the metal investigated was charged to a negative potential of 15 volts to insure saturation. Due to the influence of the light, negative electrons were emitted from the metal. These were caught on an opposing Faraday cylinder of copper gauze which was connected to the electrometer. The photo-current or number of emitted electrons was taken as proportional to the deflection. Simultaneously the energy of the incident light was recorded by a second observer who noted the galvanometer deflection when the shutter was opened to admit light to the photo-cell. The gas pressure was about 0.003 mm. at the time of these measurements. For the following reasons however it is thought that the photocurrents are not appreciably influenced by this residual gas:

First. These metals have been in this particular exhausted tube for nearly two years. Repeated cuttings have been made during this time so that presumably all active gases have been removed.

Second. Neither do the surfaces change noticeably for days after a cutting, nor are the photo-currents influenced at all by repeated cuttings. In other words the photo-currents taken a minute after cutting are quite the same as the currents observed an hour after cutting.

[1] W. W. Coblentz, Bulletin Bureau of Standards, 9, 56 (1913).

THE SELECTION OF A SUITABLE SOURCE OF ILLUMINATION

An attempt was made to calibrate the energy distribution in the mercury spectrum and then use this calibration for the corresponding photo-currents, which were to be measured later. The relative energy distribution in the mercury arc spectrum was found to be so greatly modified by slight changes in external conditions that a calibration was impracticable. Voltage changes of say 5 per cent. and condensed mercury in the neck of the negative terminal or on the sides of the tube caused variations of 100 per cent. in energy measurements even when the voltage and amperage were kept as nearly constant as practicable on the usual D.C. circuit. The Nernst glower seemed quite satisfactory for constancy, but the character of the curve giving the photo-current per unit of energy as a function of wave-length changed on changing lamps or on changing the intensity of the same lamp. Throughout these measurements the thermocouple was fixed in position and covered a definite portion of the slit of the spectrometer so that the photo-current and energy determinations were made simultaneously on different portions of the same beam.

Fig. 1 shows a coulomb-calorie wave-length curve for different inten-

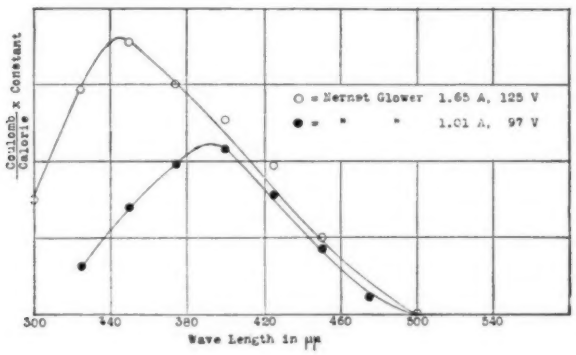


Fig. 1.

sities of the same Nernst glower, using a lithium surface aged 40 days. There were no appreciable changes in the surface in less than six or eight hours, while measurements were completed within one hour. By using the calcium-oxyhydrogen flame, the Pfund (iron) arc, the Nernst glower or the mercury arc and properly adjusting the intensity it was possible to obtain a maximum at any wave-length between 280 $\mu\mu$ and 400 $\mu\mu$. Now the intensity of the photo-current for a given surface and wave-length has been shown to be directly proportional to the intensity of the source,[1] hence any change in intensity or source should not affect the

[1] P. Lenard, Ann. d. Physik, 8, 149 (1902).

curve, for the photo-current values should increase in exactly the same ratio as the intensity. In other words the curve connecting photo-current per unit intensity and wave-length should be entirely independent of the nature or condition of the source.

These inconsistencies are due to long heat waves which are thrown into the visible or ultra-violet spectrum. Such an effect is to be expected from the phenomenon of anomalous dispersion. Fig. 2 shows two curves

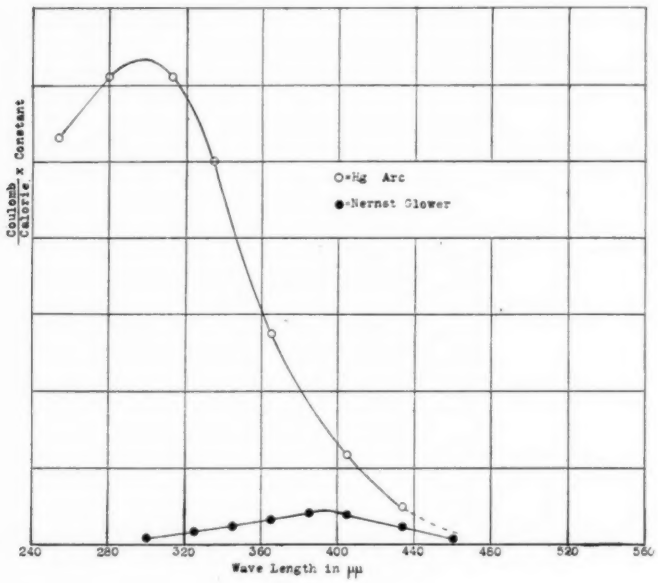


Fig. 2.

which were obtained under precisely the same conditions save for a change in the source of illumination. Now the position of each point on these curves is determined, for a given wave-length, by the quotient of photo-current and incident energy. In the case of the Nernst glower the figure shows that the energy is too large with respect to the photo-current. Since the long wave-length limit of this metal was at about 560 $\mu\mu$, the presence of long heat waves cannot influence the photo-current, but they do influence the thermopile readings. Coblentz[1] has shown that a $CuCl_2$ solution in an absorption cell may be used to remove practically all heat radiation. A repetition of the above observations using such a cell gave no change in the position of the curve for the mercury arc, but it pushed up the curve from the Nernst glower into coincidence with that from the mercury arc, in the visible spectrum. In the ultra-violet the absorption of $CuCl_2$ makes its use impracticable.

[1] W. W. Coblentz, Bulletin Bureau of Standards, 9, 93 (1913).

The figure illustrates well how completely energy distribution curves, obtained by prisms, may be falsified by these stray heat waves resulting, no doubt, from anomalous dispersion. The absorption of $CuCl_2$ begins again in the ultra-violet hence it cannot be used to prove the absence of stray radiations from the mercury arc in this part of the spectrum. Changing the intensity should however do in the case of the mercury lamp, what it was shown to do in the case of the Nernst lamp (see Fig. 1), viz., change the relative distribution of the disturbing rays if any are present. Such changes failed to modify the curve appreciably. In other words it was found that exactly the same curve would be obtained from the mercury lamp whether it was run at a low or high intensity, with or without absorbing cells.

Rough measurements of total radiation and the radiation in the visible indicated that about 0.3 of the total radiation of this mercury arc, when consuming 3.4 amperes at 112 volts, was in the visible, whereas in the case of the Nernst glower, not one tenth this fraction was in the visible. For more elaborate work on this subject see the paper of Coblentz.[1] From the above results one may conclude that there are no large stray effects to be expected in light from a mercury arc resolved by a prism, when only the more intense lines are used.

Energy Distribution in the Lines of the Mercury Arc.

By pushing the arc up to 3.6 amperes and 120 volts a fairly satisfactory condition was obtained. The heat was so intense that no mercury could collect on any part of the tube and that which would ordinarily collect in the constriction at the negative terminal was constantly vaporized; in fact the quartz was near the melting point. To prevent the destruction of the terminal seals, a strong jet of air was directed against each seal. Incidentally it might be remarked that a lamp running under these conditions generates large quantities of ozone which may have a serious physiological effect upon the observer if the gas is not constantly removed from the room.[2] Looking directly at the lamp for only a few seconds may later produce excruciating eye pain. Although the lamp had been made more nearly constant, there were still fluctuations due to slight voltage changes, inability to set on the same part of a group of lines, etc. By inserting the thermopile in the slit of the illuminator, having first separated the elements so that about one third of the resolved light passed through, and making simultaneous observations of energy and photo-currents, consistent results were obtained. An approximate

[1] W. W. Coblentz, Bulletin Bureau of Standards, 9, 93 (1913).

[2] E. O. Jordan and A. J. Carlson, Journal Amer. Med. Assn., 61, 1007 (1913).

calibration of the intensities of the principal lines at two energy consumptions is given in Table II.

TABLE II.

Wave-length in $\mu\mu$.	D_1	D_2	D_1/D_2
230.3	.10	—	—
253.5	.24	.07	3.4
280.4	.28	.02	14
312.6	1.2	.14	8.6
334.1	.71	.12	4.9
365.0	8.8	.36	24.4
404.7	5.9	.20	29.5
435.9	14.1	.35	40
546.1	24	.42	57
579.0	47	.59	80

The relative galvanometer deflections are represented by D_1 and D_2. The former corresponds to an energy consumption of 3.6 amperes at 112 volts, the latter to 2.7 amperes at 55 volts. (The wave-length settings were made at the shortest line, where there were groups of lines.) Although these relations are fairly reliable, for this lamp, it must not be supposed that they would apply to other lamps, for the values would be modified by the length of the tube, the thickness of the quartz, etc. The ratio D_1/D_2 is not constant, and as we would expect if anything like Wien's Displacement Law applies to monochromatic radiators. This irregularity of intensity increase may be seen almost as well from the photographs reproduced in Fig. 3. These were all made on the same plate

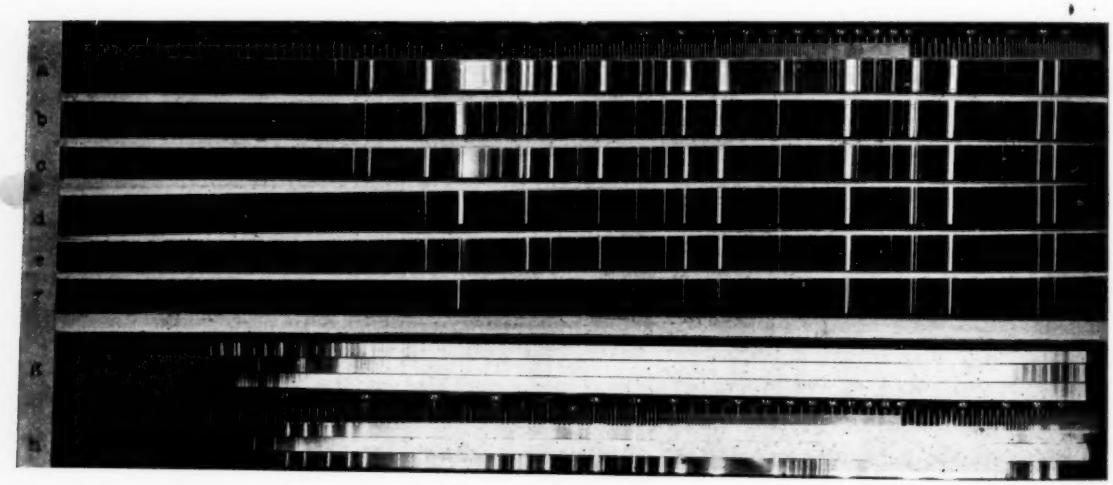


Fig. 3.

and received identical treatment in development and printing. Spectra *a*, *c*, and *e* are the same except for length of exposure. The lamp was consuming 3.4 amperes at 112 volts. Similarly *b*, *d*, and *f*, where the lamp consumed 3.2 amperes at 55 volts. The exposures in the latter case were about twenty times those in the former. If we take any line in the intense source and select an exposure of the weaker source where this line has approximately the same intensity, then compare these spectra throughout we may see the marked change in the ratio. Attention is especially directed to lines 253.5, 280.4 and 312.6 $\mu\mu$. Hence the necessity of taking photo-current and energy measurements simultaneously rather than trying to match a lamp intensity, or trying to hold it constant.

Energy at Short Wave-Lengths.

The fact that this apparatus does not give strictly monochromatic light under all conditions raises the question as to the reliability of energy determinations at short wave-lengths, where the energy is comparatively weak. From 230 $\mu\mu$ to 185 $\mu\mu$, the lower limit of adjustment of this instrument, the energy values, which were large enough to be quite definite, steadily decreased showing no indication of a distinct line. Consequently one is led to believe that most of the effect is due to stray radiation. For this reason no confidence is placed in energy readings below 230 $\mu\mu$. Additional evidence for this conclusion is contained in spectra *g* and *h*, Fig. 3, where are shown copper, aluminum and iron above, with mercury, zinc and mercury below. All are intentionally much over-exposed in the visible. Although the plate is sensitive to short wave-lengths (see zinc 210 $\mu\mu$) the mercury source shows nothing below 225 $\mu\mu$, indicating that in the case of mercury, stray light may be as strong or even stronger than the monochromatic light, thus giving only uniform darkening on the negative. A special spectrograph, having a shorter air path and lower wave-length limit, failed to show lines in this region. Again the absorption of quartz begins to be important at these short wave-lengths, so that energy measurements made with a thermopile outside a photo-cell and used when comparing photo-currents of metals inside will be in error due to the unknown absorption of the quartz in the cell window. For these reasons the curves are not continued in this region. Until the above difficulties are cleared up, one may question very strongly, any curves extending below 230 $\mu\mu$, if taken with this type of apparatus.

Results and Discussion.

The results are shown in graphic form in Fig. 4, where photo-currents per unit incident energy are plotted as ordinates and wave-lengths as

abscissæ. The surfaces were all newly formed by cutting in vacuo. The values are all plotted to the same scale and if plotted on Fig. 2 would extend to only one fifth the height shown here. The work on lithium is a repetition, in part, of a former experiment which has been reported recently.[1]

The surprising result is that new surfaces formed in this way do not show the normal effect, described by Pohl and Pringsheim, when unpolarized light is used at normal incidence. The sodium and potassium show definite maxima. In the case of sodium, this maximum is at the selective resonance point. For potassium it is below the selective resonance wave-length but is more pronounced than that for sodium.

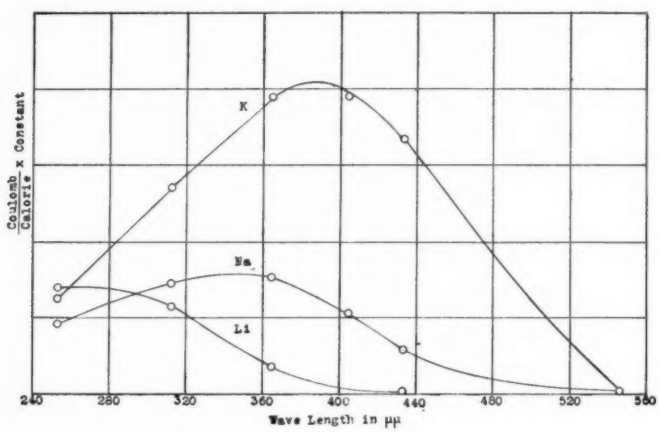


Fig. 4.

Here we have evidence from experiments on sodium and potassium, in addition to those previously reported for lithium, that the definition of the normal and selective effect is not complete, for under conditions which should, according to Pohl and Pringsheim's definition, give only the normal effect, there appears a property which they associate only with the selective effect. Since practically all properties of the light source have been considered, viz., intensity, polarization, wave-length, angle of incidence and penetration, without being able to successfully differentiate these phenomena, it seems now that attention may well be directed to other phases of the problem. It is very probable that surface conditions may play an essential part. The surfaces here investigated were made by cutting with a razor-edge tool, thus giving a mirror-like surface. Such surfaces, while they have a mirror-like appearance, must possess some different characteristic from those upon which the usual normal photo-current energy curves have been taken.

[1] R. A. Millikan and W. H. Souder, Proc. Natl. Acad. Sc., 2, 19 (1916).

The previous work on lithium bears out the idea that at least part of the distinguishing characteristics of the normal and selective effects are located in the surface of the metal. A factor of this nature might show these results in accord with those of other observers.

Attention should be called to the fact that these new surfaces are photo-sensitive, especially at wave-lengths near their selective point maxima, despite the evidence submitted by Küster,[1] Fredenhagen,[2] Wiedmann and Hallwachs,[3] purporting to show pure metal surfaces not photo-active.

I have to thank Mr. Otto Koppius for able assistance in taking many of the observations.

I am especially indebted to Professor Millikan for his direction and criticism throughout the investigation.

Summary.

1. The mercury arc is the only source found free from stray effects when used with the Hilger monochromatic illuminator. This statement applies to the more intense lines only, where, if stray effects be present, they are negligibly small.

2. New surfaces of lithium, sodium and potassium are found to be photo-active.

3. A maximum suggesting the selective effect for sodium and potassium has appeared under conditions which are supposed to yield only the normal effect.

Ryerson Physical Laboratory,
The University of Chicago,
April 10, 1916.

[1] H. Küster, Physik. Zs., Leipzig, 15, 68 (1914).
[2] K. Fredenhagen, Ibid., 15, 65 (1914).
[3] G. Wiedmann and W. Hallwachs, Ber. D. physik. Ges., 16, 107 (1914).

SOME REMARKS ON THE MICA X-RAY SPECTROMETER OF W. S. GORTON.[1]

BY MANNE SEIGBAHN.

MR. W. S. GORTON has used the mica X-ray spectrometer, introduced by de Broglie and Bohmann, in an investigation of the tungsten spectrum. As there appears in this memoir a series of results which are inconsistent with our actual knowledge I have reviewed the conclusions of Mr. Gorton, and find that they are based on false presumptions. By a graphical method Mr. Gorton has measured a great many lines in the tungsten spectrum, with an accuracy —as he says —of 0.5 per cent. But as the following calculations show there are in reality—in the domain of small angles—much greater errors, which may lie in the inaccurate method.

From his measurements Mr. Gorton concludes that the mica has 4 reflecting sets of planes parallel to the cleavage face. The distances at two of these give no simple rational relations. In the author's opinion they indicate "a substance which is mixed in with the mica and scattered non-uniformly through it." There is also another peculiarity in Table I., which may be mentioned: only one single line is ascribed to any other order than the *first*, though one would expect to find at least the stronger lines in several orders.

All these contradictions can be simply eliminated by another interpretation of the numerical results than that given in the latter part of Mr. Gorton's paper. A glance at the excellent reproduction in the Journal de Physique of the spectrogram obtained by M. de Broglie with a mica-reflector shows that there are at least 6 orders of the Pt-line; further it is to be seen and it is also remarked by de Broglie that the odd orders are essentially stronger than the even orders. M. de Broglie says that the dispersion of mica is 1/358 of the dispersion of rock-salt, which would give a value for $2d$ of about 20×10^{-8}, whereas Gorton gives the four values:

Series.	$2d$.
1	3.86×10^{-8} cm.
2	6.38×10^{-8}
3	5.66×10^{-8}
4	10.70×10^{-8}

[1] PHYS. REV., March, 1916.

These results are obtained because Gorton ascribes all lines to a first-order spectrum, whereas they really belong to the second, third, fourth and fifth orders. The first-order lines are missing; perhaps because they are covered by the central blackening.

TABLE I.

Sin θ Int.	Line, Order.	$2d \times 10^8$.
0.377 s.	$\alpha_1 5$	19.5
0.329 s.	$\beta_1 5$	19.4
0.320 f.	$\beta_2 5$	19.4
0.304 v.f.	$\alpha_1 4$	19.4
0.285 f.	$\gamma_1 5$	19.7
0.266 f.	$\beta_1 4$	19.2
0.258 v.f.	$\beta_2 4$	19.2
0.230 s.	$\alpha_1 3$	19.2
0.226 v.f.	$\gamma_1 4$	19.4
0.210 s.	$\beta_1 3$	19.1
0.195 m.	$\beta_2 3$	19.1
0.172 v.f.	$\gamma_1 3$	19.1
0.140 m.	$\alpha_1 2$	21.0
0.120 m.	$\beta_1 2$	21.3
0.117 f.	$\beta_2 2$	21.2
0.102 v.f.	$\gamma_1 2$	21.5

In the table are given the values of sin θ, the corresponding line and its order, and the calculated value of $2d$. The notations and the values of λ are my own[1] which correspond to the values of Gorton[2] fairly well as Table II. shows. These lines are the strongest in the tungsten spectrum

TABLE II.

Siegbahn-Friman.		Gorton.	
α_1	1.471	a	1.466
β_1	1.278	b	1.275
β_2	1.241	d	1.237
γ_1	1.095	g	1.094

(as in all others). They also coincide with the strongest lines according to the indications given in Table I. of Gorton's paper. As our Table I. shows, all the four lines α_1, β_1, β_2, γ_1 occur in the second, third, fourth and fifth orders and give values of $2d$ which agree fairly well. There is

[1] Siegbahn and Friman, "Uber die Hochfrequenzspektra (Z-Reihe) der Elemente Ta bis Bi," Ann. d. Phys., 1916.

[2] PHYS. REV., February, 1916.

however a definite systematic change. The lack of agreement at small angles (in the second order) is easily understood.

The varying intensity of one and the same line on the various plates (ex. 0.332 f., 0.328 m., 0.329 s., 0.327 m. for the line β_1), due to accidental faults in the crystal, is a decided objection to the use of the mica spectrometer.

LUND, PHYSICAL LABORATORY,
April, 1916.

NOTE ON BLACK-BODY BRIGHTNESS EQUATIONS BASED ON EQUIVALENT WAVE-LENGTHS.

BY HERBERT E. IVES AND E. F. KINGSBURY.

IN a recent paper Foote and Fairchild[1] develop equations for the luminous flux emitted by the black body by considering the flux a function of the equivalent wave-length. This mode of attack presupposes the existence of exact data derived by the more straightforward and logical method of integrating the product of emission by luminosity at each wave-length. The formulæ obtained by this indirect method are, however, considerably shorter than the formulæ necessary for the exact integration,[2] and nearly as accurate.

The object of this note is to give the appropriate constants to represent by this new form of equation the results of using the spectral luminosity curve obtained by the present writers.[2, 3]

Following the line of thought of Foote and Fairchild we note that the Wien equation for monochromatic intensity gives the following:

$$\frac{d \log J}{dT} = \frac{c_2}{T^2} \frac{1}{\lambda}, \tag{1}$$

where J is monochromatic intensity, T is absolute temperature, c_2 is the black body constant, and λ is the wave-length observed. Now the full process of integration mentioned above shows that for J we may substitute L, the luminous flux, provided we confine ourselves to a narrow range of temperature. The wave-length λ then becomes the equivalent wave-length λ_e for that temperature. This wave-length is not a constant but varies slowly with the temperature, and it is found that this variation may be quite closely represented by the equation.

$$\lambda_e = a + \frac{b}{T} + \frac{c}{T^2}. \tag{2}$$

[1] Foote and Fairchild, "Luminosity of a Black Body and Temperature," Scientific Papers, Bureau of Standards, No. 270, March 21, 1916.

[2] Kingsbury, "A Spectral Luminosity Curve and its Use," PHYSICAL REVIEW, February, 1916, p. 161.

[3] Ives and Kingsbury, "Physical Photometry with a Thermopile Artificial Eye," PHYSICAL REVIEW, November, 1915, p. 319.

If this is substituted back in (1) we obtain as the luminous flux equation

$$\frac{d \log L}{dT} = \frac{c_2}{aT^2 + bT + c}. \tag{3}$$

If b and c are taken as zero this is the Wien equation, which has been used in connection with the total light from the black body under the name of the Rasch equation.[1] If c alone is equal to zero, integration gives the Goldhammer or Nutting[5] black body equation. When all three constants have real values there are *three* solutions, as follows:

$$L = A \left(\frac{T + \frac{b - \sqrt{b^2 - 4ac}}{2a}}{T + \frac{b + \sqrt{b^2 - 4ac}}{2a}} \right)^{\frac{c_2}{\sqrt{b^2 - 4ac}}} \qquad \text{if } b^2 - 4ac > 0, \tag{4}$$

$$L = A' e^{\frac{2c_2}{\sqrt{4ac - b^2}} \tan^{-1}\left(\frac{2aT + b}{\sqrt{4ac - b^2}}\right)} \qquad \text{if } b^2 - 4ac < 0, \tag{5}$$

$$L = A'' e^{-\frac{2c_2}{2aT + b}} \qquad \text{if } b^2 - 4ac = 0. \tag{6}$$

Foote and Fairchild mention only the first of these, probably because the equivalent wave-length equation, which they derive by averaging several experimental spectral luminosity curves, happens to have the arrangement of signs and relative values of constants for which it is the solution.

On undertaking to put into this form the data calculated and tabulated by Kingsbury,[2] embodying the experimental work of the writers, it was found that the equivalent wave-length equation was

$$\lambda_e = .545 + \frac{77}{T} - \frac{6000}{T^2}, \tag{7}$$

so that $b^2 - 4ac$ is also positive for these data.

Using (7), equation (4) becomes

$$L = 23{,}934 \left(\frac{T - 55.853}{T + 197.138} \right)^{104.221}, \tag{8}$$

which gives the light watts per steradian per unit solid angle with very great accuracy (within $\frac{1}{2}$ per cent.). From this the candlepower per square centimeter may be derived by dividing by the mechanical equivalent of light.

[1] Rasch, Annalen d. Phys. (4), 14, p. 193, 1904.

[2] Nutting, "Luminosity and Temperature," Bull. Bur. Standards, No. 6, No. 3, p. 342, 1909.

Of the three expressions (4), (5) and (6), the third is by far the simplest, being in fact simpler to work with than the Nutting equation, which has the same number of parameters. The condition of its use ($b^2=4ac$) is not fulfilled by (7), but its simplicity has suggested that it be looked upon merely as another variation of the Wien or Rasch equation such as might have been suggested by knowledge of the manner in which that equation failed. We find that a slight variation of the constants needed for (7) gives in the following equation

$$L = 24{,}000e^{-\frac{1}{.00003795T+.00250}}, \qquad (9)$$

a working formula correct to about $\frac{1}{2}$ per cent. over the range from 1200–3000°.

The United Gas Improvement Company,
Physical Laboratory,
May 19, 1916.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THE LAW OF ABSORPTION OF X-RAYS AT HIGH FREQUENCIES.[1]

BY ALBERT W. HULL AND MARION RICE.

IT has been shown, from Barkla's absorption data and Moseley's table of wave-lengths, that the coefficient of absorption of all metals varies approximately as the cube of the wave-length, except in the immediate vicinity of one of the characteristic wave-lengths of the metal. The experimental data extends over a range of wave-lengths from 4 to 0.5 Å.U. approximately, but the law has frequently been extrapolated to very short wave-lengths and used as a measure of wave-length. It is important to know how far such extrapolation is justified.

The measurements given below were made on narrow portions of a beam of "white" radiation from a tungsten target, dispersed by a rock-salt crystal and isolated by a very narrow slit in the lead face of the ionization chamber. The absorbing sheets were 15 cm. from this slit, so that the amount of fluorescent and scattered radiation entering the chamber was negligible.

The energy taken from the beam by the absorbing sheets consisted, therefore, of two parts:

1. That which was transformed into energy of a different form or different wave-length, such as heat, fluorescent radiation, corpuscular radiation.

2. That which was re-emitted as radiation of the same wave-length, viz., the scattered radiation. The observed absorption coefficient μ/ρ may therefore be written

$$\frac{\mu}{\rho} = \frac{\tau}{\rho} + \frac{\sigma}{\rho},$$

where τ is what may be called the transformation coefficient and σ the coefficient of scattering.

On the simple electromagnetic theory we should expect σ to be independent of wave-length and proportional to the number of scattering electrons per unit volume, *i. e.*, to the density approx., so that σ/ρ should be a universal constant. This hypothesis is substantiated, within the limit of experimental error, by

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 20–21, 1916.

Barkla's measurements. If we assume that the other part of the absorption, the "transformation coefficient," varies as the cube of the wave-length, eq. 1 becomes $\mu/\rho = a\lambda^3 + b$, where a is constant for a given absorber between its absorption bands, and b is the same for all substances and all wave-lengths.

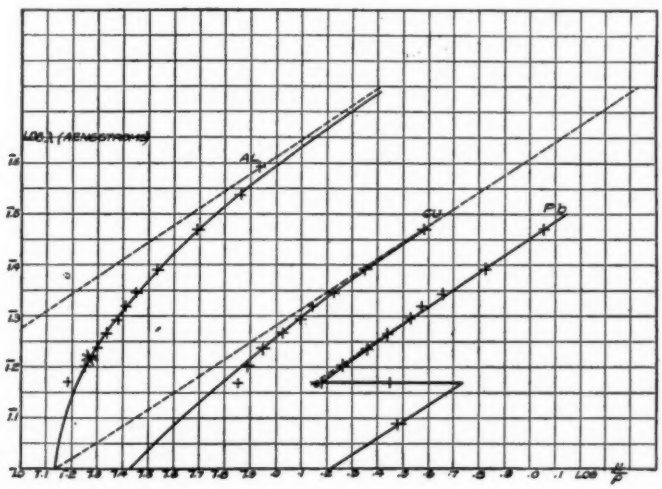
Taking a from Barkla's data on long wave-length radiations, and $b = 0.12$, the observed absorption coefficients for aluminum and copper should be given by

$$\left(\frac{\mu}{\rho}\right)_{Al} = 14.9\lambda^3 + 0.12,$$

$$\left(\frac{\mu}{\rho}\right)_{Cu} = 150.\lambda^3 + 0.12,$$

where λ is in Ångströms.

These equations are plotted in the figure (full lines), and agree with the experimental values within experimental error (the errors were rather large for the shortest and longest wave-lengths measured, on account of small deflec-



Mass Absorption Coefficient (μ/ρ) for Al, Cu, and Pb, between $\lambda = 0.12$ and $\lambda = 0.39$ Aengstroms.

Full lines = theoretical curves for complete absorption coefficient.

Broken " = theoretical curves for "corrected absorption" or "transformation" coefficient.

* = Rutherford's value for γ rays.

Fig. 1.

tions). Rutherford's value for the absorption in aluminum of the shortest γ-rays from radium B, viz., $(\mu/\rho)_{Al} = 0.19$ for $\lambda = .164$ A.U., is also shown in the figure. It falls satisfactorily on the curve.

For lead, the region investigated includes one of the characteristic absorption bands of lead. Photographs of the spectrum through a lead sheet showed that this band, which is due to the excitation of the K fluorescent radiation of lead,

begins at $\lambda = 0.149$ Å.U. For wave-lengths longer than this, the absorption obeys the equation $(\mu/\rho)_{Pb} = 430\lambda^3 + 0.12$ (full curve). The value of $a = 430$ is subject to some error on account of the difficulty of measuring the thickness of the lead sheet. For wave-lengths shorter than 0.149 the data is not sufficient to determine the law, but it is evident that extrapolation of the above equation is not justified.

If, instead of dealing with the coefficient of total absorption, as above, we calculate the "corrected absorption coefficient" or "transformation coefficient," by subtracting $\sigma/\rho = 0.12$ from the observed values of μ/ρ, we have for all substances and all wave-lengths thus far investigated the very simple law

$$\frac{\tau}{\rho} = a\lambda^3,$$

where a is a constant for each substance over the entire range between its absorption bands. This law is shown graphically for aluminum and copper (broken lines) in the figure.

Wave-length.	Mass Absorption Coefficient.					
Ångstroms.	Al.		Cu.		Pb.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0.392	0.860	1.02				
0.343	0.726	0.721				
0.294	0.493	0.499	3.84	3.94	11.1	11.04
0.245	0.342	0.339	2.24	2.33	6.7	6.44
0.221	0.283	0.281	1.70	1.74	4.63	4.76
0.208	0.255	0.254	1.39	1.47	3.70	3.99
0.196	0.243	0.232	1.27	1.25	3.40	3.36
0.184	0.218	0.213	1.07	1.06	2.71	2.80
0.172	0.199	0.196	0.91	0.88	2.32	2.31
0.160	0.178	0.181	0.79	0.74	1.82	1.88
0.147	0.154	0.167	0.71	0.60	1.50	
					2.80	
0.122					3.00	